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REDUCTION OF SULFATE EMISSIONS IN BLEACHED SOFTWOOD KRAFT PULP MILL

Master's Programme in Chemical, Biochemical and Materials Engineering
Major in Biomass Refining

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 22nd March 2019

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Abstract

The aim of this thesis was to examine where the pulp mill sulfate emissions are formed and ways to reduce them. Sulfate emissions increase the water salinity and may increase eutrophication. Sulfate emissions of pulp mill are mainly caused by recovery boiler fly ash purging and the use of sulfuric acid in pH adjustment. Especially softwood pulp mills have excess sulfur in sodium and sulfur balance, since tall oil production requires sulfuric acid. The conventional way to reduce the excess sulfur is to purge part of recovery boiler fly ash, which includes sodium sulfate.

In the experimental study, several process variables for the reduction of sulfate emissions were calculated. These variables were the replacement of sulfuric acid by hydrochloric acid in pH adjustment, integrated chlorine dioxide plant, carbon dioxide semi acidulation of tall oil, replacement of aluminum sulfate by polyaluminum chloride in water treatment, fly ash treatment and internal sulfuric acid production from non-condensable gases. The effect of liquor heat treatment and green liquor stripping and carbonation was calculated for the capacity increase of sulfuric acid plant.

Five cases were composed based on the calculated process variables, which represented a feasible pulp mill main dimensioning balances. These cases were; Case 1: only chemical replacements, Case 2: sulfuric acid plant, Case 3: integrated chlorine dioxide plant, Case 4: integrated chlorine dioxide plant and sulfuric acid plant and Case 5: integrated chlorine dioxide plant and sulfuric acid plant with lignin separation and green liquor stripping and carbonation.

It was concluded that sulfate emissions were reduced, when sulfur input decreased, the sulfur cycle was more closed or sulfur-containing chemicals were replaced by other chemicals. The reduction of sulfate emissions reduced also the make-up chemical consumption. Cases 4 and 5 had the lowest sulfate emissions. Case 2 had the lowest make-up chemical consumption.

Keywords Pulp mill, Sodium/Sulfur-balance, Sulfate emissions

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Tiivistelmä

Tässä diplomityössä tutkittiin sellutehtaan sulfaattipäästöjen muodostumista ja niiden vähennyskeinoja. Sulfaattipäästöt aiheuttavat vesistöissä suolaantumista ja saattavat lisätä rehevöitymistä. Sellutehtaan sulfaattipäästöt aiheutuvat pääasiassa soodakattilan lentotuhkan poistamisesta sekä rikkihapon käytöstä pH:n säätökemikaalina. Etenkin havusellutehtailla rikkitase on ylijäämäinen, sillä mäntyöljyn valmistuksessa tehtaan kemikaalikiertoon lisätään rikkihappoa. Ylijäämärikkiä on perinteisesti hallittu poistamalla soodakattilan lentotuhkaa, joka sisältää pääasiassa natriumsulfaattia.

Työn kokeellisessa osassa laskettiin kirjallisuusosassa esiteltyjen vähennyskeinojen vaikutusta sulfaattipäästöihin. Näitä vähennyskeinoja olivat rikkihapon korvaaminen suolahapolla pH:n säätökemikaalina, klooridioksidin valmistus (integroidulla) suolahappomenetelmällä, mäntyöljyn esipalstoitus hiilidioksidilla, vedenpuhdistuksessa käytettävän alumiinisulfaatin korvaaminen polyalumiinikloridilla, lentotuhkan käsittely sekä sisäinen rikkihapon valmistus tehtaan hajukaasuista. Rikkihapon valmistuksen kapasiteetin nostoa varten laskettiin myös lipeän lämpökäsittelyn ja viherlipeän karbonoinnin vaikutus.

Näiden vähennyskeinojen pohjalta laskettiin viisi skenaariota, jotka esittivät vaihtoehtoisia mitoituksia sellutehtaalle. Nämä skenaariot olivat; 1: ei isoja investointeja sulfaattipäästöjen vähentämiseksi 2: rikkihappolaitos 3: integroitu klooridioksidilaitos 4: integroitu klooridioksidilaitos ja rikkihappolaitos 5: skenaario 4 ligniinin erotuksella ja viherlipeän karbonoinnilla.

Sulfaattipäästöt vähenivät, kun sisään tuleva rikkimäärä natrium-rikkitaseessa pieneni, rikkikiertoa suljettiin tai kun sulfaattia sisältäviä kemikaaleja korvattiin vaihtoehtoisilla kemikaaleilla. Sulfaattipäästöjen vähentäminen johti korvauskemikaalien kulutuksen pienenemiseen. Skenaariot 4 ja 5 tuottivat alhaisimmat sulfaattipäästöt. Sulfaattipäästöjen vähentäminen johti myös korvauskemikaalien kulutuksen pienenemiseen. Alhaisimmat korvauskemikaalimäärät olivat skenaariossa 2.

Avainsanat Sellutehdas, sulfaattipäästöt, Natrium/Rikki-tase

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Espoo, 22nd March 2019

Oskari Kilpi

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ABBREVIATIONS

ADt	Air dried tonne (of pulp)
BAT	Best available technology
COD	Chemical oxygen demand
CNCG	Concentrated non-condensable gases
CTO	Crude tall oil
DNCG	Diluted non-condensable gases
ECF	Elementally chlorine free
EOP	Pressurized alkaline peroxide bleaching stage
LEL	Lower explosion limit
LHT	Liquor heat treatment
NCG	Non-condensable gases
NPE	Non-process elements
PAC	Polyaluminum chloride
SOG	Stripper off gases
TRS	Total reduced sulfur
UEL	Upper explosion limit

1 Introduction

Sulfate (SO_4) compounds are salts of sulfuric acid (H_2SO_4). Sulfuric acid is used in pH adjustment, tall oil production and in chlorine dioxide (ClO_2) production in pulp mills. The use of sulfuric acid leads to sulfate emissions in pulp mill wastewater. (Chen, 1998) Another major source of sulfate emissions is the removal of sodium sulfate (Na_2SO_4) from the recovery cycle due to excess sulfur (Siren, 2013). Sulfate emissions increase the water salinity and may increase eutrophication (Ratava, 2013). WHO guideline for maximum sulfate content in drinking water is 250 mg/l (Bowell, 2004). In old pulp mills, sulfate emissions in effluent can be up to 1500 mg/l. Sulfates have not been considered as an effluent parameter of a pulp mill. Therefore, sulfates are seldom removed in the biological waste water treatment (Chen, 1998). However, sulfate emissions are more commonly investigated from the mining industry point of view (Bowell, 2000).

Sulfate emissions of mining industry have been present in Finnish media. As a result, there has also been public discussion of sulfate emissions originated from the forest industry. The environmental load of Finnish forest industry has decreased during the last decades due to tightened legislation. However, there has not been environmental limit for sodium and sulfur compounds in effluents (Kara, 1992). Nonetheless, because of the increased environmental awareness, limit for sulfate emissions has been set for new pulp mill projects (Itä-Suomen Aluehallintovirasto, 2017). In order to reach the limit, pulping technology solutions that are not widely used in conventional Kraft pulp mills are required.

This thesis investigates the sulfate emissions in a bleached softwood Kraft pulp mill. The aim of this thesis is to explain the origin of the sulfate emissions and how to

reduce the emissions by process design. This thesis focuses on the methods that are applied or investigated in forest industry. Therefore, biological methods for sulfate removal are not included in this thesis. This thesis is divided into two parts, the literature part and the experimental study. The literature part describes Kraft pulp mill unit operations in terms of sulfate emissions. The experimental study is based on balances that are calculated for different scenarios.

Literature part

2 Sulfur in Kraft pulping

The main objective of Kraft pulping is to separate lignin from cellulose and hemicellulose. In process wise, Kraft pulp mill can be divided into two main lines: fiber line and chemical recovery line. The pulp is produced in the fiber line, and the pulping chemicals are recovered and the organic residual of wood is utilized in energy production in the recovery line. Due to energy production in the recovery boiler, kraft pulp mills have an energy surplus. (Virkola, 1983) Figure 1 describes the Kraft pulp process.

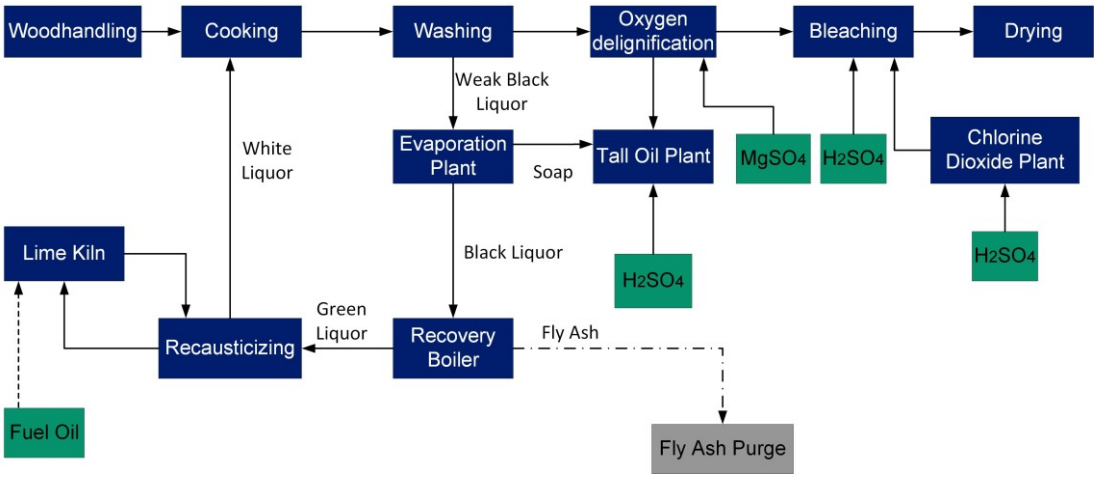

Figure 1. Simplified block diagram of a softwood Kraft pulp mill with the main sulfur inputs (green) and outputs (gray).

2.1 Fiber line

In the fiber line, wood logs are debarked and chipped in the woodyard. The residual bark is utilized in energy production. Wood chips are cooked in the alkaline cooking liquor, referred as white liquor. The main cooking chemical components of white liquor are sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The aim of the cooking is to separate lignin from cellulose and hemicellulose. Most of the lignin is dissolved into the cooking liquor and the residual lignin results in a brown color of the unbleached Kraft pulp. After cooking, the brown stock pulp is separated from the cooking liquor and washed. In order to produce bleached pulp, the brown stock is oxygen delignified and bleached. After bleaching the pulp is dried in a drying machine or pumped to paper or board mill. (Virkola, 1983)

2.2 Recovery line

The residual cooking liquor containing the organic content of wood and residual cooking chemicals is referred as black liquor. Weak black liquor is fed from the pulp washing to the recovery line, where the cooking chemicals are recovered in order to make the Kraft pulping economically feasible. The weak black liquor is concentrated in an evaporation plant and burned in a recovery boiler. (Virkola, 1983)

In addition to energy production, the recovery boiler has an important role in a Kraft pulp mill: the recovery of sodium (Na) and sulfur (S). Combustion of black liquor generates molten smelt, which is fed to dissolving tank. The smelt is mixed with diluted white liquor in the dissolving tank, producing green liquor. Green liquor includes sodium carbonate (Na_2CO_3), sodium sulfide (Na_2S) and sodium hydroxide (NaOH). (Virkola, 1983) (Blackwell, 1998)

Green liquor is regenerated into white liquor in a causticizing plant. Sodium carbonate, which is the main component of green liquor, reacts with calcium oxide

(CaO) producing sodium hydroxide and calcium carbonate $CaCO_3$. Calcium carbonate is regenerated to calcium oxide (CaO) in a lime kiln. Pulping by-products, such as turpentine and tall oil are separated in the recovery line. Turpentine is condensed from the volatile compounds formed in cooking, and tall oil is produced from softwood soap, which is separated from the black liquor. (Virkola, 1983)

2.3 Role of sulfur in Kraft pulp mill

Sulfur is present in the white liquor. The ratio of effective chemicals, NaOH and Na_2S, is controlled by a parameter called sulfidity, which is defined by the following equation:

$$\text{Sulfidity } [\%] = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH}} \cdot 100\% \quad (1)$$

Sulfidity increases during the cooking, since NaOH is mostly consumed by the cooking reactions, whereas only 20 – 30% of Na_2S is consumed. Sulfidity also varies between different mills and over time and because of the chemical losses. Normal sulfidity level is 25 – 45%, depending on wood species and region. Typical sulfidity level in softwood pulping is from 35 to 40%. The sulfidity is slightly higher in the Nordic countries than in the North American mills (Andersson, 2014) (Gustafsson et al., 2011) (Saturnino, 2012).

Higher sulfidity protects the carbohydrates and accelerates the cooking reactions, thus increasing the yield and delignification. High sulfidity also has a positive impact on strength properties of pulp. On the other hand, too high sulfidity leads to increased amount of non-condensable gases (NCG) and increases the risk of corrosion. (Gustafsson et al., 2011) (Virkola, 1983) (Sixta, 2006)

S/Na_2-ratio for sulfidity of 35 – 40% is between 0.3 and 0.4. S/Na_2-ratio must be kept in the typical level of the cooking method to ensure the optimal pulp quality and regeneration of chemicals. Sulfidity is affected by S/Na_2-ratio, but also causticizing degree. If the causticizing degree drops, the sulfidity increases, yet the S/Na_2-ratio remains constant. (Pikka, 1979)

3 Effect of sulfate emissions on water systems

Soluble sulfate salts, such as sodium sulfate (Na_2SO_4) increase the water salinity. The more saline waste water has a higher density than lake water. Due to the density differences, water forms easily two layers: saline water in the bottom and less saline water above. This phenomenon is referred as stratification, which decreases the natural water mixing with the bottom and the surface layer. (Ratava, 2013)

Sulfates also have an indirect role in the internal loading of a lake. Biomass originated from organic content, such as algae, is stored into sediments in the lake bottom. The decomposition of the organic material consumes oxygen. If the water is layered due to stratification, the oxygen will be completely consumed from the lake bottom, which results in hypoxia. In hypoxia, sulfates cause disturbance in the iron cycle and reduces the iron compounds, which leads to the phosphorous release. (Zak et al., 2006) (Smodlers & Roelofs, 1993) Since phosphorous is often a limiting nutrient in the lake water, the increase in phosphorous content may increase the internal loading. This results in an increased eutrophication. (Laukkanen et al., 2013) Although sulfates itself are non-toxic, the sulfate reducing bacteria may reduce sulfate in the anaerobic conditions. The reduction of sulfate to sulfide results in toxic hydrogen sulfide (H_2S). (Siren, 2013).

4 Sodium and sulfur balance

Since sodium and sulfur are the main elements of the pulping chemicals, sodium and sulfur balance is essential for controlling the chemical streams of the mill. Because the alkali amount is kept almost constant, sodium balance has a direct impact on the liquor reserves. Therefore, liquor reserves increase when sodium balance is positive. When sulfur balance is positive, the sulfur emissions increase, since sulfur always develops towards the state where the inflow and outflow streams are equal. In liquid streams, sodium and sulfur are usually removed in the same ratio as they exist in the liquor. (Pikka, 1979) (Saturnino, 2012)

Although the majority of pulping chemicals are recovered, a small amount of the chemicals are lost in the processes. The recovery degree corresponding to sodium and sulfur is up to 97% in modern bleached Kraft pulp mill. These chemical losses are formed through many streams, such as liquor spills, residuals in pulp, dust, effluents and stack gases. Those losses are replaced by make-up chemicals. The sodium and sulfur balance of the mill defines the make-up chemical.
(Saturnino, 2012) (Blackwell, 1998)

The most typical make-up chemicals are NaOH and Na_2SO_4, yet Na_2CO_3 can be also used. Previously, Na_2SO_4 was commonly used as a make-up chemical when both sodium and sulfur losses were higher. The higher chemical losses were caused by higher amount of spills and washing losses. Due to the more closed recovery cycle, the addition of Na_2SO_4 may increase the excess sulfur. NaOH can be used as a make-up chemical when the sulfur content in Na/S-balance is already high. (Gustafsson et al., 2011) (Saturnino, 2012) (Andersson, 2014)

4.1 Sulfur inputs to pulp mill

Sulfur enters the process with wood, water and chemicals. The chemical composition of wood depends on the wood species and the place of growth. The most common wood species in Scandinavia are scots pine and birch (Chirat et al., 2011). According to Meier et al. (2013), the sulfur content of wood varies between 74 and 120 mg/kg, when the median was 75.5 mg/kg. Finnish lake water contains small amounts of sulfur, mainly sulfates. The average sulfate content in Finnish lakes between 2012 and 2017 was 16 mg/l (Suomen ympäristökeskus, 2018).

In addition to make-up chemicals and sulfuric acid, several smaller chemical inputs exist. Magnesium sulfate ($MgSO_4$) is added to oxygen delignification to protect the fibers (Suess, 2010). Aluminum and iron based sulfates are used in the water treatment plant as a coagulation chemicals (Hynninen, 2008). Sulfamic acid (NH_2SO_3) is used in acid cleaning of evaporators (Wekesa et al., 2014).

In the recausticizing plant, a little stream of calcium compounds is removed with green liquor dregs, lime mud and other losses, such as spills. Make-up lime is added to replace the chemical losses of calcium compounds. The main component of lime is oxidized calcium (CaO) – however, it also includes small amount of other compounds, such as sulfur. According to Kontu (2010), the sulfur content in make-up lime was 84 mg/kg. According to Andersson (2014), the sulfur input from make-up lime in Skoghall mill was 0.07 kg S/ADt (Air dried ton). Furthermore, if fuel oil is used as the lime kiln fuel, it increases the sulfur input. (Kontu, 2010)

4.2 Sulfur in the pulp mill recovery cycle

Sulfur is present in the various forms in the mill liquor cycle. In addition to NaOH and Na_2S, white liquor includes small amounts of sodium sulfate, sodium sulfite (Na_2SO_3), sodium carbonate and and sodium thiosulfate ($Na_2S_2SO_3$). (Sixta, 2006)

Black liquor includes residual cooking chemicals and sulfur-based compounds in various forms. In the black liquor combustion, sodium sulfate is reduced to sodium sulfide. The amount of Na_2SO_4 being reduced to Na_2S is described by the reduction degree:

$$\text{Reduction degree } [\%] = \frac{Na_2S}{Na_2S + Na_2SO_4} \cdot 100\% \quad (2)$$

Combustion of black liquor forms flue gases, which consist of water, carbon dioxide, carbon monoxide, hydrogen, nitrogen and sodium and sulfur compounds. Flue gases include also fly ash, which is removed from the flue gases by electrostatic precipitators. The recovery boiler fly ash is typically added to strong black liquor from the evaporation plant. The fly ash recovery to the strong black liquor enhances the chemical recovery efficiency. This mixture is referred as firing black liquor, which is burned in the recovery boiler. (Juvonen, 2004) (Hupa, 1993) (Vakkilainen, 2008)

4.2.1 Non-Condensable Gases

Sodium sulfide decomposes and sulfide-ions and methoxyl groups of lignin reacts together during the cooking. This process generates odorous, sulfur-rich gases, referred as Non-Condensable Gases (NCG). A part of those compounds are released during cooking, whereas another part is combined to the black liquor. The combined part is released during the processes where the black liquor is treated, such as brown stock washing and evaporation plant. (Seppälä et al., 2001)

NCG compounds include Total Reduced Sulfur (TRS)-compounds, such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3)**.** Based on the gas concentration, NCGs are divided to Diluted Non-Condensable Gases (DNCG) and Concentrated Non-Condensable Gases (CNCG). (Bordado & Gomes, 2001) (Heinola et al., 2013) (Seppälä et al., 2001)

The concentration of DNCGs must be kept below the Lower Explosion Limit (LEL), since above the LEL the concentration may cause an explosion. When the concentration is kept low, DNCGs can be used as combustion air. The concentration of CNCGs must be kept above the Upper Explosion Limit (UEL), since below the UEL the concentration may cause an explosion. Therefore, DNCGs and CNCGs have a separate collection systems. NCGs are usually collected and incinerated in an NCG boiler, recovery boiler, power boiler or lime kiln. The incineration of NCGs in the recovery boiler increases sulfate content and decreases carbonate content in the fly ash. When the carbonate is fully consumed, the excess sulfur generates SO_2, which increases the recovery boiler emissions. If the recovery boiler emissions are already high, it is recommended to incinerate the NCGs in another place. (Heinola et al., 2013) NCGs can be utilized in the sulfuric acid production. Internal sulfuric acid production decreases the sulfur input in the sodium and sulfur balance. (Wimby et al., 2017)

4.2.2 Methanol liquefaction

Stripper off gases (SOG) refers to non-condensable gases originated from the stripping of foul condensates. SOG includes methanol (30 – 50%), TRS compounds and terpenes. Stripper off gases can be incinerated or fed to the methanol plant, where the liquefied methanol is produced. Non-condensable gases formed in the

methanol liquefaction can be collected to CNCG system. (Heinola et al., 2013) Liquefied methanol can be incinerated as a support fuel. A novel technology is to produce commercial grade methanol by methanol purification. Methanol purification requires sulfuric acid, and the by-product of purified methanol is ammonium sulfate ($(NH_4)_2SO_4$), which can be utilized as a fertilizer. (Pehu-Lehtonen & Sjögård, 2018)

4.3 Sulfur outputs from the pulp mill

Sulfur exits the mill in gaseous or liquid form. Air emissions consist of mainly on TRS compounds and sulfur dioxide. Sulfur exists in the effluents from the process areas, where sulfuric compounds are used. Liquor spills includes various sulfur compounds. (Saturnino, 2012)

In Scandinavian softwood pulp mills, the common problem is high sulfur to sodium ratio, since tall oil production requires sulfuric acid, which increases the sulfur input in the Na/S-balance. Since sulfur balance always develops to the state where input and output are balanced, the increased sulfur input leads to increased output. Due to the environmental regulations and economic reasons, pulp mills have been forced to reduce the sulfur emissions to atmosphere. Furthermore, more developed pulp washing technology has decreased the sulfur losses with the pulp leaving the washers.

The traditional way to control sodium and sulfur balance is to remove a part of recovery boiler fly ash, which includes mainly sodium sulfate and sodium carbonate. However, the fly ash purging leads to sodium losses, which increases the make-up chemical consumption. Also, the composition of fly ash slightly varies, which makes the controlling of Na/S balance difficult. (Andersson, 2014) (Gustafsson et al., 2011) (Saturnino, 2012) (Wimby et al., 2017)

4.4 Effect of sodium and sulfur balance on chloride and potassium balance

Closing of the Na/S-balance increases the enrichment of Non-Process Elements (NPE), especially chloride (Cl) and potassium (K) to the recovery cycle. High Cl and K content increases corrosion problems in the recovery boiler. (Tran, 2004) Chloride is originated from the wood chips and process water, whereas potassium is mainly originated from the wood chips. In addition, make-up chemicals may include small amounts of NPEs (Saturnino, 2012).

In modern pulp mills, the alkaline filtrate from bleach plant can be recovered to brown stock washing in order to minimize the water consumption. This leads to higher amount of chlorides in the recovery cycle. (Johakimu et al., 2016) Similar to excess sulfur, chloride and potassium balance can be controlled with fly ash purging (Tran, 2004). Furthermore, a small part of Cl and K is removed with green liquor dregs and spills. (Lundström, 2007)

5 Sources and reduction of sulfate emissions

There are two dominant causes for sulfate emissions from pulp mill: the fly ash purging in order to control the chemical balances, and sulfur compounds in bleaching effluents. (Siren, 2013) (Chen, 1998) Since fly ash purging for the removal of excess sulfur leads to sulfate emissions, the causes for excess sulfur are described in this chapter. This chapter describes more accurately where the sulfate emissions are originated and the ways to reduce the sulfate emissions. Furthermore, process design methods to control and reduce the emissions are presented.

5.1 pH adjustment

The chlorine dioxide bleaching stages are performed in acidic conditions (Sixta, 2006). The pH is usually lowered with sulfuric acid, which leads to sulfate emissions (Chen, 1998). Sulfuric acid is usually purchased to the mill. Typical H_2SO_4 concentration on mill scale is 98 wt-%. (Suess, 2010)

Sulfuric acid can be replaced by hydrochloric acid (HCl), and HCl is used for pH adjustment in some mills (Pelkonen, 2012). The use of HCl can be even more economically feasible, if it is by-product of the chlorine dioxide plant. The potential problem with HCl is the corrosion of the equipment (Suess, 2010).

5.2 Chlorine dioxide production

Chlorine dioxide (ClO_2) is the main bleaching chemical in Elementary Chlorine Free (ECF) bleaching, and it is always produced at the mill due to its unstable nature. Although chlorine dioxide can be prepared with several methods, all the methods are based on the reduction of sodium chlorate ($NaClO_3$) in acidic conditions. Chlorine dioxide production generates salt cake as a by-product. The composition and amount of salt cake varies depending on the production method used. The

production method is selected on the basis of investment costs and sodium and sulfur balance of the mill. Table 1 presents the production methods described in this thesis. The production methods can be divided to non-integrated and integrated methods. In the non-integrated methods, sodium chlorate is delivered to the mill, whereas in the integrated process sodium chlorate is prepared along the chlorine dioxide production. (Saturnino, 2012) (Sixta, 2006)

Table 1. Methods for chlorine dioxide production. Adapted from (Sixta, 2006).

Production method	**NaCl** ($t / tClO_2$)	**Cl_2** ($t / tClO_2$)	**Na_2SO_4** ($t / tClO_2$)	**H_2SO_4** ($t / tClO_2$)
Integrated R6	0.95	0.90	0	0
Non-integrated R8	0	0	1.36	0.11
Non-integrated R10	0	0	1.06	0

5.2.1 Non-integrated process

In the non-integrated chlorine dioxide process, $NaClO_3$ is purchased to the mill as a solid crystalline or as a concentrated (40 – 45%) aqueous solution. Sodium chlorate is reduced with methanol (CH_3OH), hydrogen peroxide (H_2O_2) or sulfur dioxide. Methanol is the most common reducing agent in ClO_2 production. (Sixta, 2006)

The most typical ClO_2 non-integrated production methods are R8 and R10. The advantage of R10 is the higher sodium and sulfur recovery and smaller amount of effluent than R8. The R8 method produces sodium sesquisulfate ($Na_3H(SO_4)_2$) salt cake as a by-product, which is practically the mixture of sodium sulfate and sulfuric acid. The acidic salt cake must be neutralized before the utilization or disposal. The R8 can be updated to R10, where the salt cake is filtered to neutral Na_2SO_4 and acidic sodium bisulfate ($NaHSO_4$). The acidic sodium bisulfate can be reused in the chlorine dioxide plant. (Siren, 2013) (Saturnino, 2012)

Sodium sulfate can be either dissolved in waste water or utilized as a make-up chemical. If the sodium sulfate is dissolved in waste water, it increases the sulfate emissions. On the other hand, if it is used as a make-up chemical, it may increase the excess sulfur in the Na/S-balance. The excess sulfur may lead to increased fly ash purging, which also increases the sulfate emissions. Furthermore, the recycling of salt cake to pulp mill may increase the chloride content in the recovery cycle. (Siren, 2013) (Saturnino, 2012) If the salt cake is dissolved in waste water, it has no effect on Na/S-balance of the recovery area. However, if the fly ash is also removed due to Cl and K balance, the fly ash removal cannot be reduced although the sulfur input decreases. (Siren, 2013)

5.2.2 Integrated process

Integrated chlorine dioxide plant uses HCl as a reducing agent. The process includes chlorate plant, chlorine dioxide plant, hydrochloric acid plant and chlorine alkali plant. $NaClO_3$ is prepared at the mill by the electrolysis of sodium chloride and water. NaCl and water are also used as raw materials also in the chlorine alkali plant, which produces elemental chlorine (Cl_2) and hydrogen (H_2) for HCl plant. Chlorine alkali plant yields NaOH as a by-product, which can be utilized in the pulp mill. Chlorine dioxide is generated in the ClO_2 plant by the reaction of HCl and $NaClO_3$. NaCl is produced as a by-product salt, which can be utilized in the $NaClO_3$ production. The excess chlorine is utilized in the HCl plant. The block diagram of the integrated process is presented in Figure 2.

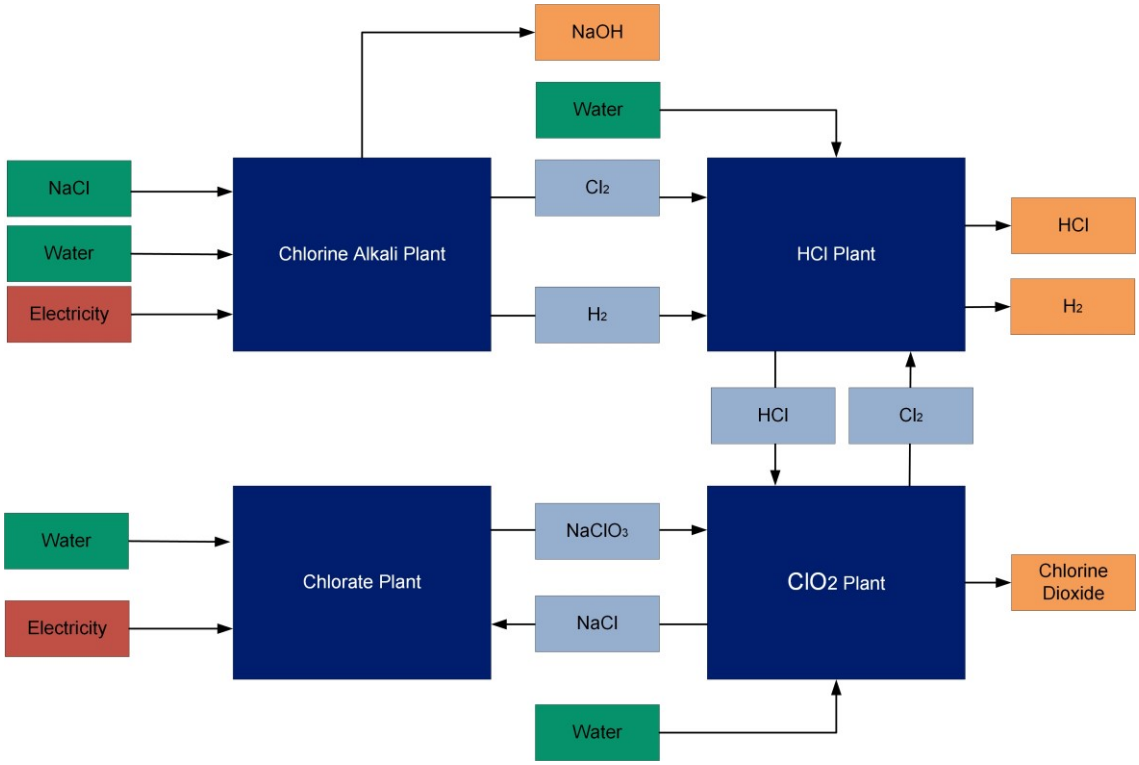

Figure 2. Block diagram of an integrated chlorine dioxide plant. Adapted from (Chirat et al., 2011)

Advantages of the integrated process are the raw materials that are safe and easy to handle. Furthermore, the production of NaOH as a by-product reduces the need for purchased NaOH. Since H_2SO_4 is not used, sulfur-based by-products are not generated. (Fredette, 1996) The disadvantages of the integrated process are higher investment costs and larger space required at the mill site. (Fredette, 1996) (Chirat et al., 2011) Furthermore, the amount of elemental chlorine has been relatively high, up to 11 – 23% in the range of ClO_2 production in old chemical plants (Sixta, 2006). However, due to enhanced technology, the amount of Cl_2 has decreased to 0.2 g/l of Cl_2, which results in about 2% of the ClO_2 production. (Chemetics, 2012)

5.3 Fly ash purging

The main components of fly ash are sulfate (SO_4), sodium (Na), carbonate (CO_3), potassium (K) and chloride (Cl). Sodium is mainly in the form of sodium sulfate and sodium carbonate. (Minday et al., 1997)

Fly ash is purged to control the Na/S-balance. Another reason for fly ash purging is the removal of Cl and K (Tran, 2004). The purging results in sulfate emissions (Siren, 2013). Therefore, if the fly ash is purged due to excess sulfur, the sulfur input must be decreased (Saturnino, 2012). Considering that the fly ash purge is caused by excess Cl and K, ash treatment could decrease the sulfur losses. With ash treatment, Cl and K are removed more selectively, whereas Na and S are recycled back to the recovery cycle. (Tran, 2004)

5.4 Removal of chloride and potassium by ash treatment

In order to decrease the sodium losses and sulfate emissions without the enrichment of chloride and potassium due to closed recovery cycle, chloride and potassium must be removed – the easiest way to remove them is separation from the fly ash. Several ash treatment processes with different principles for chlorine and potassium removal are available: ash leaching, evaporation-crystallization, freezing-crystallization and ion exchange. Although the processes are different, the basic principle of the first three processes is similar since those processes are based on solubility differences. (Goncalves et al., 2008) Ash leaching and evaporation-crystallization are the dominant ash treatment methods in the industry. Evaporation-crystallization has a higher theoretical performance than ash leaching. However, it requires a greater number of equipment and is more expensive to install, operate and maintain than ash leaching. (Valmet, 2018) Generally, the NPE removal efficiency varies depending on ash concentration, solubility of individual

salts and solid-liquid separation degree. (Goncalves et al., 2008) The recovery and removal efficiencies of commercially used methods are presented in Table 2.

Table 2. Removal and recovery efficiencies of commercial ash treatment technologies. The values are based on the literature and the material that Pöyry Finland Oy possesses.

Method	Cl removal %	K removal %	Na recovery %	S recovery %
Evaporation/Crystallization	90 - 96	87 -92	85 - 88	90 - 91
Freeze crystallization	90	75	70	75
Ash leaching	44 - 98	44 - 98	55 - 87	55 - 90
Ion exchange	90 - 95	95 - 99	70	75

5.4.1 Evaporation-Crystallization

Evaporation-crystallisation process utilizes the relatively low solubility of Na_2SO_4. First, the fly ash is dissolved in water or process condensate. Then, the mixture is evaporated. Due to the lower solubility, Na_2SO_4 crystallizes first. The solid phase containing the most of Na_2SO_4 is filtered and recycled to the liquor cycle. The residual liquid rich in Cl and K, referred as mother liquor, is recycled to the crystallizer, yet a small portion is led to sewer to remove the Cl and K. Several industrial installations and machine suppliers exist for this technology. (Tran, 2004)

More advanced evaporation-crystallization technology developed by Veolia produces valuable fertilizer from the side streams. Enhanced Chloride Removal Process (EPCR™) produces potassium sulfate (K_2SO_4) as a by-product. The process includes a conventional crystallizing unit, where Na_2SO_4, burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) and Na_2CO_3 are crystallized. The second stage includes an adiabatic flash crystallizer, which operates at a low temperature. Since the solubility of potassium salts, such as glaserite ($3\ K_2SO_4 \cdot Na_2SO_4$) is decreased in the lower temperature, chlorides can be purged and glaserite can be centrifuged. Water is added to the melting unit, which results in selective dissolution of K_2SO_4 and Na_2SO_4, leaving

K_2SO_4 in a solid phase. Potassium sulfate is then centrifuged and dried, whereas chloride rich stream is purged. (Begley et al., 2017)

5.4.2 Ash Leaching

Ash leaching is based on the lower solubility of Na_2SO_4 than Cl and K. First, the ash is mixed with water in the leaching tank to form slurry. The slurry is pumped with a slurry pump to a decanter centrifuge, which forms two phases, solid and liquid. The solid part includes more Na_2SO_4 whereas the liquid part is enriched with K and Cl. The solid part is recovered to the process, while the liquid part (leachate) is recycled back to the leaching tank. Part of the liquid part is removed from the system as the means of K and Cl removal. (Hart et al., 2010) (Tran, 2004) Ash leaching can be operated to either optimize the Cl and K removal or the recovery of Na and S. The more water added, the more ash dissolves which enables the higher amount of chloride and potassium removal. On the other hand, greater amount of water dissolves also more sodium and sulfur, which increases losses. (Valmet, 2018)

5.4.3 Freeze crystallization

Freeze crystallization is based on the massive decrease in sodium sulfate dehydrate ($Na_2SO_4 \cdot 10\ H_2O$) solubility at low temperatures. When the temperature decreases below 30-°C, Na_2SO_4 precipitates to $Na_2SO_4 \cdot 10\ H_2O$ crystals, whereas Cl and K remains dissolved in solution. Therefore, the two phases can be separated, and the purified sodium sulfate crystals can be returned to the process. The liquid phase is purged in order to remove Cl and K. Sulfuric acid may be added to the process to improve the sodium recovery. (Tran, 2004)

5.4.4 Ion exchange

Ion exchange treatment, Precipitator Dust Purification (PDP™) has been developed by Eco-Tec and Paprican. Ash is dissolved to warm water and led through fixed-bed packed with an amphoteric resin, which contains anion and cation exchange groups. Regeneration of the resins is performed with countercurrent flow. (Tran, 2004) Since chloride-ions (Cl^-) are the only monovalent anions in the fly ash mixture, the resins absorb sodium chloride in preference to sodium sulfate and sodium carbonate. Although the method is highly selective with chloride removal, the problem with ion exchange has been the low potassium removal. (Ferreira et al., 2003) (Tran, 2004) However, Noram PDP™ System could reach potassium removal of 80% simultaneously with 80 – 97% chloride removal and over 90% sulfate recovery. (Foan, 2016)

On the contrary to other techniques, sodium sulfate is returned to the process in liquid phase. Therefore, this method requires spare capacity in the evaporation plant. If the evaporator capacity is a bottleneck, this may require investment on pre-evaporation stage to minimize the water load on the existing evaporators. The advantage of the ion exchange process is the lower steam consumption than in the evaporation-crystallization process. (Tran, 2004)

5.5 Electrochemical treatment of fly ash

One possibility to handle the fly ash is an electrochemical treatment, where sodium sulfate (Na_2SO_4) can be separated to NaOH and H_2SO_4. Electrolytic split of the fly ash reduces make-up chemical costs and sulfate emissions. Since the fly ash contains potassium, also KOH is produced. (Siren, 2013)

However, the method has several disadvantages. According to Öhman et al. (2014), the increase in electricity demand was 8 – 30% of the normal electricity consumption of the mill. Furthermore, the payback times were up to nine years (Öhman et al., 2014). The concentration of sulfuric acid produced was reported to be low (8 – 10%), which makes it too diluted for tall oil production. However, the diluted acid could be utilized in pH adjustment. (Siren, 2013) If the acid could be used in chlorine dioxide production, additional filters are required since the H_2SO_4 stream includes large amount of sodium sulfate. (Öhman et al., 2014)

5.6 Tall oil production

Kraft pulping of softwood converts the resin acids and fatty acids of wood to their sodium salts, which are the main components of soap. Since black liquor contains soap, it foams easily, which leads to production and quality losses. Therefore, the soap is separated from weak and intermediate black liquor and refined to crude tall oil (CTO), which is an important by-product of softwood pulp mills. Crude tall oil is produced in the tall oil plant, which is usually located in the evaporation plant. Tall oil can be produced via batch or continuous process. Crude tall oil production increases the cost-competitiveness of the mill, and it can be refined to various products in the chemical industry. (Aro & Fatehi, 2016) (Tikka et al., 2002) (Laxen & Tikka, 2008)

Since the soap density is lower than black liquor density, the soap is separated from the black liquor via settling and overflow. Then, the soap is acidulated with sulfuric acid. The mixture is decanted to different layer based on density differences. The spent acid is neutralized and led to the evaporation plant, thus the sulfur goes to the recovery cycle. The crude tall oil production may consume 180–300 kg of sulfuric acid per ton of crude tall oil. The acid consumption depends on the black liquor content of the soap. (Laxen & Tikka, 2008) (Aro & Fatehi, 2016)

Due to the high amount of sulfuric acid consumption, alternative acidulation chemicals have been tested, and some of them are also applied at industrial level. In the two stage acidulation, sulfuric acid is not used in the first acidulation step. Carbon dioxide (CO_2) and sodium bisulfite ($NaHSO_3$) has been investigated on semi acidulation. (Laxen & Tikka, 2008)

In the carbon dioxide semi acidulation, CO_2 is converted to carbonic acid (H_2CO_3). Carbonic acid decreases the pH of the solution and enables the reaction of tall oil soap. However, since the carbonic acid production is limited in the tall oil reactor, pH of the mixture does not decrease enough. Therefore, sulfuric acid is still required about half of the amount that would be required for the traditional acidulation process. (Laxen & Tikka, 2008)

Sodium bisulfite ($NaHSO_3$) semi acidulation has been investigated (Laxen & Tikka, 2008). Sodium bisulfite is usually collected from the flue gas scrubber of NCG boiler (Salmenoja, 2009)**.** Sodium bisulfite is produced from sulfur dioxide from the stack gases and used as a reducing agent in bleaching (Suess, 2010). The sulfur dioxide gas is absorbed in sodium hydroxide. The advantage of the process is that no fresh sulfur is added to the process. Since the sulfur dioxide content varies in the flue gases, and the flue gases include only a slight amount of SO_2 in a modern mill, the mill cannot produce enough bisulfite. (Laxen & Tikka, 2008)

5.7 Wash loss

The purpose of pulp washing is to separate the black liquor from the brown stock. In order to minimize the environmental impact, the aim of pulp washing is to use a minimal amount of water. This is done by utilizing the washing filtrates in a counter-current recirculation and recovering all of them to the evaporation plant. Furthermore, since the black liquor is concentrated in the evaporation plant, a

minimal water amount is desired. Greater amount of wash water requires more capacity in the evaporation plant. (Kopra & Dahl, 2017) (Pikka, 1979)

The amount of those washable components that remain in the pulp after washing is referred as wash loss. Wash loss can be described as the amount of sodium in the pulp, expressed as kg of Na_2SO_4 / oven-dried ton of washed pulp. Another analyzing method of wash loss is the chemical oxygen demand (COD). (Kopra & Dahl, 2017) (Sillanpää, 2005) Since the wash loss results in sodium and sulfur losses, it increases the sulfur input. (Pikka, 1979)

5.8 Magnesium sulfate in oxygen delignification

The purpose of oxygen delignification is to continue lignin removal before bleaching. Since pulp cannot be cooked to too low kappa without a yield decrease, the lignin degradation is continued in the oxygen delignification stage, which is more sensitive than cooking. Furthermore, oxygen stage decreases the consumption of bleaching chemicals, such as chlorine dioxide (ClO_2). (Isotalo et al., 1983)

Although oxygen is a mild oxidant, the reduction of oxygen generates peroxide and hydroxide radicals, which are strong oxidants. Those radicals split the carbohydrates, which decreases viscosity and yield of pulp. Magnesium sulfate ($MgSO_4$) is used in the oxygen delignification to protect the fibers. (Suess, 2010) (Isotalo et al., 1983) For the same reason, it can be also used in the pressurized alkaline peroxide (EOP) bleaching stage (Thakore, et al., 2005). If magnesium sulfate is used in bleaching, it increases the sulfur content in bleaching effluent. In the oxygen stage, it increases the sulfur input. (Persson, 2015)

Magnesium hydroxide ($Mg(OH)_2$) has been studied to replace the $MgSO_4$, since the use of magnesium hydroxide would decrease the chemical costs. According to (Bouchard & Wang, 2011), the results were poor in the oxygen stage, whereas it was found to be suitable and cost-effective chemical for cellulose protection in EOP stage. (Thakore et al., 2005)

5.9 Liquor spills

Liquor spills are originated from process equipment or overflows, and results in chemical losses and emissions to water. Liquor spills can be formed in wherever liquor is circulating in the mill. Spill recovery and collection reduces the spills. Sodium and sulfur usually occur in the same ratio in the spill liquor in which they exist in black liquor. Liquor spills results in sulfur losses, which increases the make-up chemical consumption. (Pikka, 1979) (Saturnino, 2012)

5.10 Internal sulfuric acid production

In the case of excess sulfur in Na/S-balance, one way to control the excess sulfur is to produce sulfuric acid from the sulfur-containing CNCGs. Internal sulfuric acid production decreases the need for ash purging, since it decreases the excess sulfur in Na/S-balance. Few industrial installations of pulp mill internal sulfuric acid plant exist. (Wimby et al., 2017) (Valeur et al., 2001) (Humalajoki & Kiuru, 2018)

First, CNCGs are collected and incinerated in a dedicated incinerator. In the incinerator, TRS compounds are oxidized into SO_2 with high efficiency. Then, the flue gas from the incinerator is led to a catalytic converter, where SO_2 is oxidized into SO_3 according to reaction 3. Vanadium pentoxide (V_2O_5) is used as a catalyst. Since the reaction is exothermic, the process generates heat. (Wimby et al., 2017) (Valeur et al., 2001)

$$SO_2 + \frac{1}{2}O_2 \leftrightarrow SO_3 + Heat\ (3)$$

In the third part of the process, the flue gases are cooled in the partial condenser. SO_3 reacts with H_2O producing sulfuric acid according to reaction 4.

$$SO_3 + H_2O \leftrightarrow H_2SO_4 + Heat\ (4)$$

SO_2 containing flue gases are led to bisulfite scrubber, where they are washed with sodium hydroxide. The flue gas scrubber produces sodium bisulfite ($NaHSO_3$).

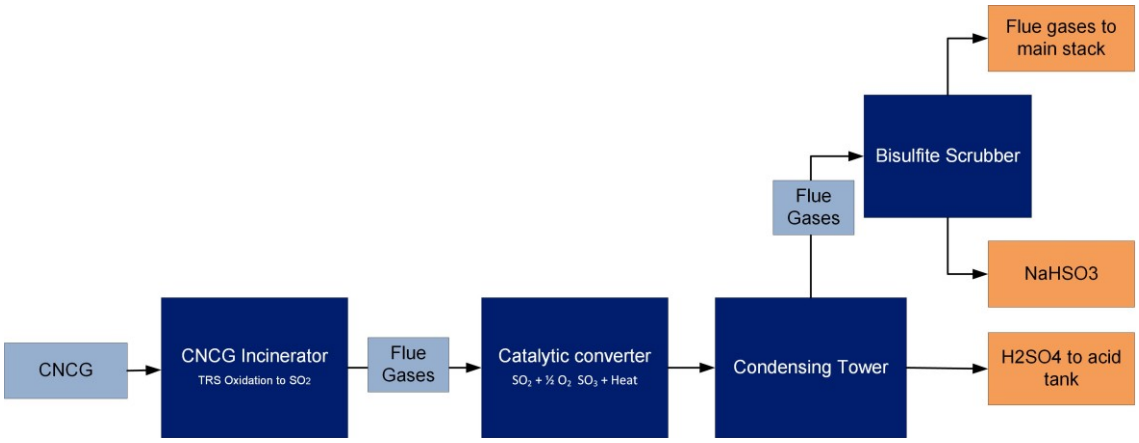

Figure 3. Simplified block diagram of sulfuric acid production. Adapted from (Wimby et al., 2017).

The concentration of the produced acid is 40 – 60 weight-percent. The final concentration depends on the partial pressures of SO_2 and H_2O in the flue gas. If higher concentration is required, the acid can be further concentrated to 93%. The corrosion risk decreases with higher concentration. (Valeur et al., 2001) (Wimby et al., 2017)

The sulfuric acid production is limited by mass flow and sulfur content of CNCG, which are dependent on sulfidity, pulp yield, cooking conditions and black liquor dry solids. The typical content is 1.5 – 7 kg S/ADt. The sulfur content of CNCG can be increased by green liquor stripping and liquor heat treatment. (Valeur et al., 2001)

5.10.1 Green liquor stripping and carbonation

Green liquor stripping and carbonation can be utilized to maximize the sulfuric acid production (Valeur et al., 2001). In the green liquor carbonation, Na_2S is separated from green liquor. The method is based on Sivola-Lurgi-method, which has several variations. Instead of Kraft mills, the carbonation is often used in sulfite mills, since the green liquor carbonation is a common method for regenerating the cooking chemicals in sulfite pulp mills. However, the green liquor stripping and carbonation can also be applied on Kraft pulping. Since the method is not essential for the chemical recovery cycle in Kraft mills, stripping and carbonation can be applied to small amount of green liquor stream, when the major part of green liquor is remained the same as without the stripping and carbonation. (Ingruber, 1985) (Fuller, 1981) (Sivola, 1956)

Although there are different variations of green liquor stripping and carbonation, the principle is similar. First, the green liquor is contacted with flue gases, which includes carbon dioxide. Na_2CO_3 and Na_2S in green liquor react with CO_2 producing sodium hydrosulfide (NaHS) and sodium bicarbonate ($NaHCO_3$) according to Reactions 5 and 6.

$$2\,Na_2S + CO_2 + H_2O \leftrightarrow 2\,NaHS + Na_2CO_3 \quad (5)$$

$$Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2\,NaHCO_3 \quad (6)$$

NaHS and 2 $NaHCO_3$ react together in the stripping column according to Reaction 7. The reaction produces hydrogen sulfide and sodium carbonate.

$$NaHS + NaHCO_3 \leftrightarrow H_2S + Na_2CO_3 \quad (7)$$

Hydrogen sulfide, which is one of the key components of NCGs, can be oxidized to sulfuric acid (Valeur et al., 2001). Sodium carbonate can be causticized to pulping liquor or utilized in $NaHCO_3$ production. (Fuller, 1981) (Ingruber, 1985)

5.10.2 Liquor heat treatment

The increase in black liquor dry solid content raises the viscosity above 60% dry solid content. The increased viscosity impedes the pumping. Furthermore, the increased viscosity causes problems in the evaporation plant, since the black liquor sticks to the heat surfaces. Higher temperature decreases the viscosity and enhances the liquor pumping. However, when the temperature rises, it reaches the boiling point at the specific concentration at the atmospheric pressure. Utilizing the pressurized tanks enables higher dry solid content of the black liquor. Another method to raise the dry solids content of black liquor without the increase in viscosity is Liquor Heat Treatment (LHT). (Nikkanen, 1993) (Parviainen et al., 2008) (Kiiskilä & Virkola, 1990)

The LHT is made by keeping the liquor at a high temperature. The typical heating temperature is around 175 – 180 °C and with the residence of time 30 min, or alternatively 190 – 195 °C and 15 min. During the heat treatment, lignin and high-molecular-weight polysaccharides are split, which reduces the viscosity permanently. (Nikkanen, 1993) Due to the viscosity reduction, LHT enables 2 – 5% higher dry solid content in the firing liquor. This reduces the SO_2 emissions and improves the energy efficiency. The LHT releases methanol and gaseous sulfur compounds, corresponding to 2–5 kg sulfur per ton of pulp produced. (Nikkanen, 1993) (Parviainen et al., 2008) This increases the amount of NCGs, which can be utilized in the sulfuric acid production. (Wimby et al., 2017)

5.11 Water treatment

Pulp production requires large amounts of water. Process water is usually mechanically and chemically treated. The quality requirements and raw water properties varies from mill to another. Usually the raw water quality requirements

in Finnish mills concern color, iron and manganese content, since they exist in the native soils. (Hynninen, 2008)

Effluent treatment is often applied as a multi-stage process. The first method is usually mechanical treatment, which includes solids removal with clarification, flotation and filtration. The main treatment is usually biological treatment, such as activated sludge process. The aim of the biological treatment is to remove non-biodegradable organic content or increase the phosphorous removal. If required, tertiary treatment is applied after the biological treatment. Chemical coagulation is found to be suitable for forest industry effluents. (Laukkanen et al., 2013) (Hynninen, 2008)

The idea of chemical treatment is to collect the smaller solid particles to generate larger flocks, since the larger blocks are easier to remove. Sulfate-based salts are used as a coagulation chemical. These salts include aluminum sulfate (Al_2SO_4) and iron sulfates ($Fe_2(SO_4)_3$ and $FeSO_4$. In addition to sulfate based salts, also FeCl and lime can be used for coagulation. (Hynninen, 2008) Polyaluminum chloride (PAC) can be used as a coagulation chemical to replace the sulfate-based chemicals. (Gao et al., 2005)

5.12 Lignin separation

Separation of lignin from black liquor enables higher pulp production if recovery boiler is a bottleneck of the pulp mill, because the lignin separation reduces the recovery boiler load. The separated lignin can be utilized as a fuel for lime kiln or as a raw material for valuable by-products of the pulp mill, thus making new revenue for the mill. (Kousini et al., 2012) The most common method for lignin separation applied in the industry is precipitation. The method is based on lignin solubility

decrease when acidity increases. The pH is adjusted with CO_2, since H_2SO_4 results in excess sulfur and HCl increases the chloride input. (Loutfi & Uloth, 1991)

One industrial application for lignin separation is the LignoBoost™ technology owned by Valmet. In the LignoBoost process, the pH is decreased with CO_2. The decreased pH leads to lignin precipitation. Then, the lignin is filtered and the filter cake is re-dispersed and acidified with H_2SO_4. In the final stage, the lignin slurry is filtered and displacement washed. (Tomani, 2010) Since the lignin separation requires H_2SO_4, it increases the sulfidity level of the mill (Partanen, 2015). With the integrated sulfuric acid plant, it is possible to compensate the increased sulfuric acid demand (Pehu-Lehtonen & Sjögård, 2018).

6 Conclusions of the literature part

Sulfate emissions are mainly originated from bleaching effluents and removal of the fly ash. Fly ash is purged to balance the excess sulfur in Na/S-balance. The excess sulfur is often caused by tall oil production in softwood mill. In addition, wash losses and spills may end up to effluent, and increase the make-up chemical consumption. Sulfuric acid plant decreases the sulfate emissions, since it closes the sulfur cycle and decreases the excess sulfur in the process. Another reason for the need of fly ash purge is the enrichment of Cl and K in the black liquor, when the recovery cycle becomes more closed. With ash treatment, Cl and K are removed more selectively whereas Na and S are recovered.

There are several solutions to reduce the sulfate emissions. Some methods, such as semi acidulation and integrated ClO_2 plant decreases sulfur input, since these methods decrease the sulfuric acid consumption. Some chemicals that cause sulfate emissions can be replaced with other chemicals. Sulfate-based salt in the chemical water treatment could be replaced by PAC. Sulfuric acid in pH can be replaced by HCl in pH adjustment. The disadvantage of HCl is an increased risk of corrosion.

Magnesium hydroxide could replace magnesium sulfate in the bleaching stage, whereas the results of using $Mg(OH)_2$ in the oxygen stage were reported to be poor. Although the usage of magnesium hydroxide could decrease the sulfate emissions, using two magnesium-based chemicals would require two chemical systems, thus increasing the complexity of the mill.

Traditional pulp mills are moving towards to biorefineries, in which more value-added by-products are produced. Producing fertilizers from recovery boiler ash or in the methanol plant would increase the revenue of the mill and reduce the sulfate

emissions to water. Lignin can be used as a raw material for various new bioproducts. Still, lignin separation requires sulfuric acid and may increase the sulfate emissions.

Experimental study

7 Introduction to experimental study

The aim of the experimental study was to explain how the sulfate emissions can be reduced by process design. A greenfield softwood Kraft pulp mill producing bleached pulp with the capacity of 1,000,000 ADt per year was used as the basis for the balance calculations. Pulp mill balances were calculated in Microsoft Excel. First, the balance was calculated for the base case (Case 0), which represented a worst case scenario: no process design to reduce sulfate load was considered.

Methods to reduce the sulfate emissions were considered as variables. The following variables were calculated: internal sulfuric acid production, integrated ClO_2 plant, HCl for pH adjusting, ash treatment, CO_2 semi acidulation in the tall oil plant and PAC as a coagulation chemical. Liquor heat treatment and green liquor stripping and carbonation were calculated for the capacity increase of the sulfuric acid plant. Furthermore, because the modern pulp mills are moving towards to carbon neutral operations, the effect of bark gas in the lime kiln fuel on sulfate emissions was calculated as a variable.

In order to explain the combined effect of particular variables presented above, several scenarios were calculated by combining the variables. These scenarios were considered as cases. The aim of the cases was to represent a feasible balance for a greenfield mill. As concluded from the literature part, the investment cost of the integrated ClO_2 plant is higher than the non-integrated plant. Furthermore, the whole new process department is required for the sulfuric acid production, which also leads to an increased investment costs. Therefore, these processes were selected to compose the first four cases: Case 1 does not require major investments in reduction of sulfate emissions, Case 2 includes the sulfuric acid plant, Case 3

includes the integrated chlorine dioxide plant and Case 4 includes both the R6 plant and the H_2SO_4 plant. Furthermore, since the new greenfield pulp mills are moving towards biorefineries which produces various bioproducts, Case 5 was calculated to investigate how much sulfate emissions can be reduced if lignin separation is used. Since lignin separation requires high amounts of H_2SO_4, the hypothesis was that several reduction methods are required. Case 5 includes lignin separation, and the sulfate emissions are decreased by integrated ClO_2 plant and sulfuric acid plant. The capacity of sulfuric acid plant is increased by green liquor stripping and carbonation. The cases are presented in Table 3.

Table 3. Cases studied in the experimental study.

Case	**Description**
Case 0	Base case
Case 1	Low investment expenditure
Case 2	H_2SO_4 plant
Case 3	Integrated ClO_2 plant
Case 4	H_2SO_4 plant + Integrated ClO_2 plant
Case 5	H_2SO_4 plant + Integrated ClO_2 plant with lignin separation

7.1 Balances and system boundaries

Main dimensioning balance included fiber and chemical balances of a pulp mill and chemical plants. Also, the capacities of the main departments were calculated. Water treatment plants and power boiler were excluded from the system boundary. The main dimensioning balance is presented in the Appendices 1–6. Main dimensioning balance included Na/S-balance and-Cl/K balance of the recovery cycle. The system boundaries and main inputs and outputs for Na/S-balance and Cl/K-balance are presented in Figure 4.

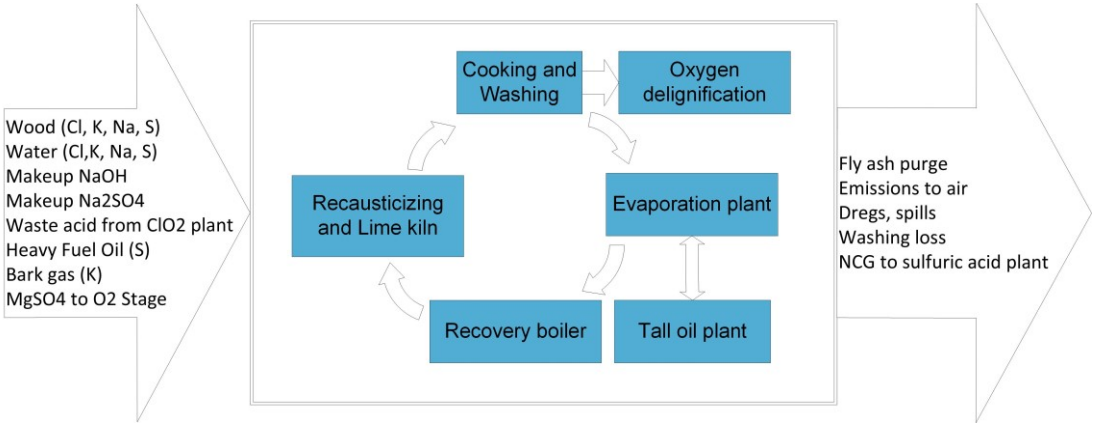

Figure 4. System boundary of Na/S-balance and Cl/K-balance.

Pulp mill sulfur balance was calculated on the basis of Na/S-balance and main dimensioning balance. The sulfur balance included the whole pulp mill, chemical plants and water treatment plants. Power boiler for biomass incineration was moved beyond the system boundary, in the case of bark being burned instead of gasified (Figure 5). Total sulfate emissions to the environment were calculated from the sulfur amount in effluent. In addition, $NaHSO_3$ emissions were also considered as sulfate emissions, since it may oxidize with chlorine dioxide.

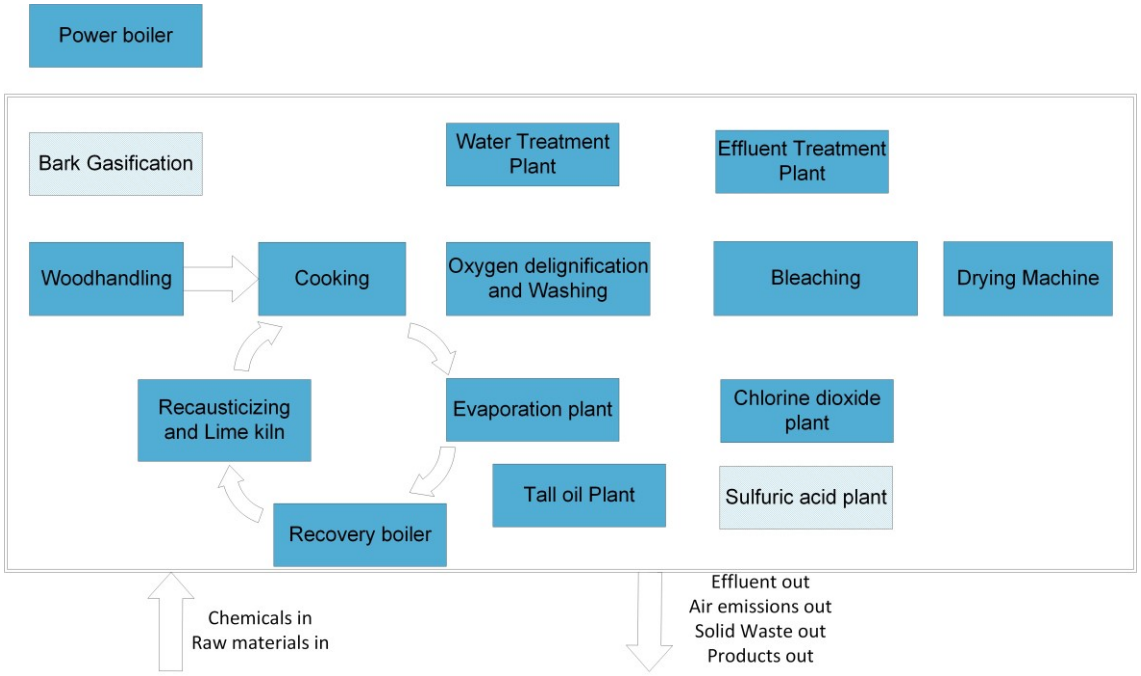

Figure 5. System boundary of the pulp mill sulfur balance.

7.2 Process description of selected pulp mill

A greenfield softwood Kraft pulp mill produces bleached pulp with the capacity of 1,000,000 ADt per year. The tall oil yield of the mill is 50 kg/ADt. The three-stage bleaching sequence is D0-EOP-D1, and the whole pulp production is dried in the drying machine. Wood dust and sludge are burned in the biomass boiler. Depending on the case, bark is burned in the biomass boiler or gasified to lime kiln fuel. Flue gas values for recovery boiler and lime kiln were taken from the upper limit of Best Available Technologies (BAT) for pulp and paper industry (Sühr et al., 2015). The furnace load of the recovery boiler is 3000 kW/m^2. Total sulfur in NCGs is estimated to be 5 kg S/ADt. Washing losses and spills are estimated to be constant in this thesis. Make-up chemicals are NaOH and Na_2SO_4. All the waste acid from the ClO_2 plant is utilized as a make-up Na_2SO_4. Cooling water and process water are mechanically treated, and the process water is further chemically treated.

The mill includes a three-stage effluent treatment plant. Primary treatment stage is mechanical treatment, an activated sludge plant is used as the main treatment and chemical coagulation is used as a tertiary treatment stage. All the effluent is led to the tertiary treatment. Aluminum sulfate is used as a coagulation chemical in the base case. The amount of waste water flow is 25 m^3/ADt, a figure presented in the BAT documentation for a typical greenfield pulp mill (Sühr et al., 2014). Since it was estimated that water lost in vaporization is 1 m^3/ADt, the amount of process water to chemical treatment is estimated to be 26 m^3/ADt. The use of sulfuric acid in water treatment and in the other departments is estimated to be 2.8 kg/ADt. The initial values are gathered from project information databases that Pöyry Finland Oy possesses. Basic operating data of the mill is presented in Table 4.

Table 4. Basic operating data for pulp mill applied in this thesis.

Raw material		
Unbarked roundwood	6 270 000	m^3sob/a
Purchased chips	620 000	m^3sob/a
Raw material distribution	67-%	Scots pine
	34-%	Spruce
Non-process elements		
Chloride content in wood	85	g/ton
Potassium content in wood	750	g/ton
Potassium content in bark gas	2700	g/ton
Cooking conditions		
Sulfidity	40	%
Cooking kappa	30	
Heavy Fuel Oil		
Lower Heating Value (LHV)	39.6	MJ/kg
Fuel oil for lime kiln	135	kg/ ton of lime
Sulfur content	1.5	%

7.3 Base case (Case O)

The base case represented a pulp mill with no process design to reduce the effluent sulfate load. The pH was adjusted with sulfuric acid, and the Na/S-balance was balanced with fly ash purging. No ash treatment was included. Heavy fuel oil was used as a lime kiln fuel, and aluminum sulfate was used in the chemical treatment of water.

As Figure 6 describes, the sulfate emissions in the base case were 119 tons of sulfate per day [t/d]. The excess sulfur in Na/S-balance was removed by fly ash purging. The ash purging led to sodium loss, which was recovered with makeup NaOH. The consumption of make-up chemicals and sulfuric acid and the key values of Cl/K-balance are presented in Table 5.

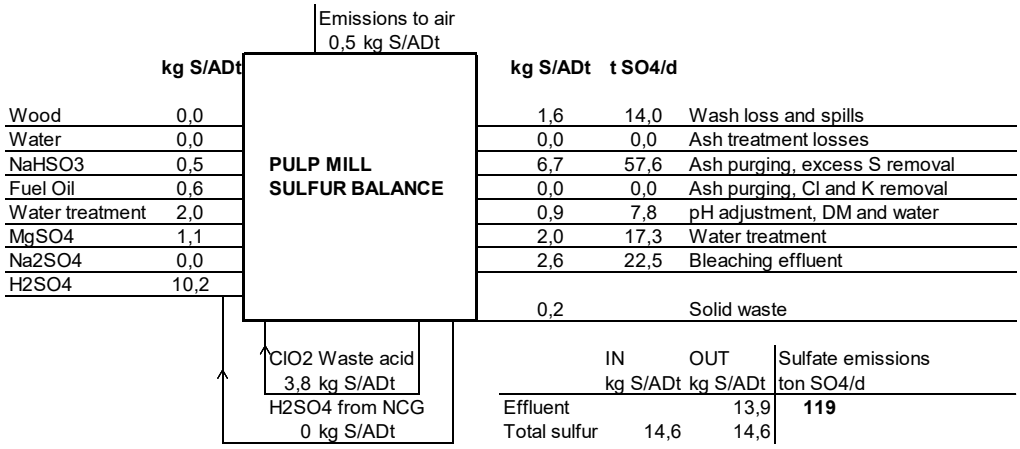

Figure 6. Sulfur balance of Case 0.

Table 5. Chemical consumptions and ash treatment data of the base case.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	268	g/ADt
Potassium In / Out	1563	g/ADt
Black liquor max Cl content	0.09	%wt
Black liquor max K content	1.09	%wt
Make-up chemicals		
Make-up NaOH	25.1	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	31.2	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8 Variables in the study

The effect of variables on sulfate emissions was compared to base case. However, it was concluded that the effect on sulfate load reduction was fixed with some variables, whereas with some other variables the reduction was dependent on another variables. Therefore, some variables seemed to be feasible only for specific cases. For instance, ash treatment reduced the sulfate emissions only if the fly ash was purged due to Cl/K balance. Those variables which required specific conditions were compared to the scenarios where they would be feasible.

8.1 Hydrochloric acid as pH adjustment chemical

Sulfuric acid was replaced by hydrochloric acid in pH adjustment. It was estimated that sulfuric acid consumption in the base case was 5 kg of H_2SO_4 /ADt in the bleaching and 2.8 kg H_2SO_4 /ADt in the other departments in the mill. The corresponding amount of HCl was calculated with the following method.

First, the amount of sulfuric acid was calculated according to the equation 8:

$$n(H_2SO_4) = \frac{m(H_2SO_4)}{M(H_2SO_4)} \quad (8)$$

Where,

$n(H_2SO_4)$ is amount of sulfuric acid [mol]

$m(H_2SO_4)$ is mass of sulfuric acid [g]

$M(H_2SO_4)$ is molar mass of sulfuric acid [g/mol]

Since H_2SO_4 is a diprotic acid, it can release two H^+-ions, whereas HCl can release only one H^+-ion. Therefore, the amount of H_2SO_4 needed is half of the amount of HCl needed. The equivalence factor for H_2SO_4 is 0.5, whereas for HCl the equivalence factor is 1.

Hence

$$m(HCl) = 2\,M(HCl)\,\frac{2\,m(H_2SO_4)}{M(H_2SO_4)} \approx 0.74\,m(H_2SO_4)\ (9)$$

As Figure 7 describes, the sulfate emissions decreased from 119 t/d to 97 t/d. However, the sulfur balance was still positive. The remaining sulfate load from the bleaching effluent was originated from $MgSO_4$ and $NaHSO_3$. The reduction of H_2SO_4 consumption can be seen on Table 6.

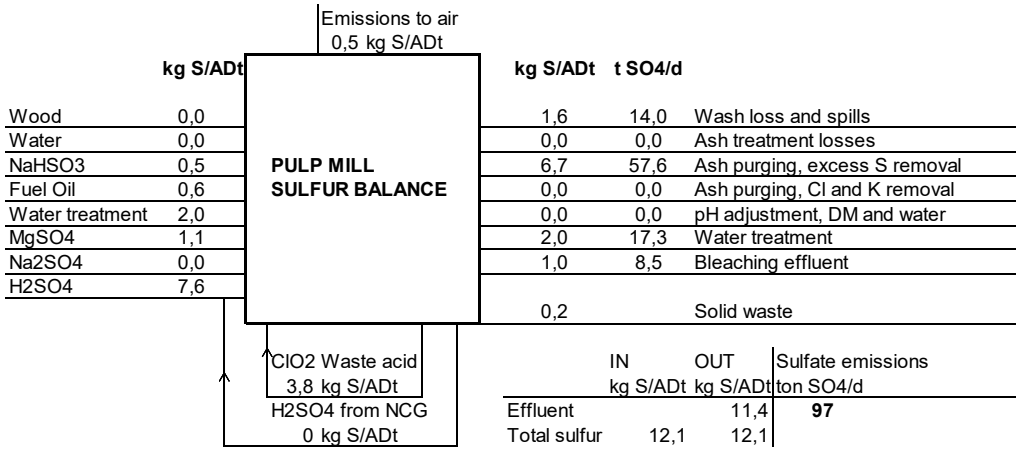

Figure 7. Sulfur balance and sulfate emissions when HCl is used in pH adjustment.

Table 6. Chemical consumption when HCl is used in pH adjustment.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	270	g/ADt
Potassium In / Out	1565	g/ADt
Black liquor max Cl content	0.04	%wt
Black liquor max K content	1.03	%wt
Make-up chemicals		
Make-up NaOH	27.5	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	23.4	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8.2 Polyaluminium chloride (PAC) as water treatment chemical

The estimated amount of coagulation chemical was 50 mg/l for process water treatment and 500 mg/l for effluent treatment. All the $Al_2(SO_4)_3$ was replaced by PAC. Figure 8 and Table 7 describes that the replacement of aluminum sulfate by PAC decreased the sulfate emissions from 119 to 102 ton/d. Since the PAC includes chlorides, it slightly increased the chloride amount in the process water.

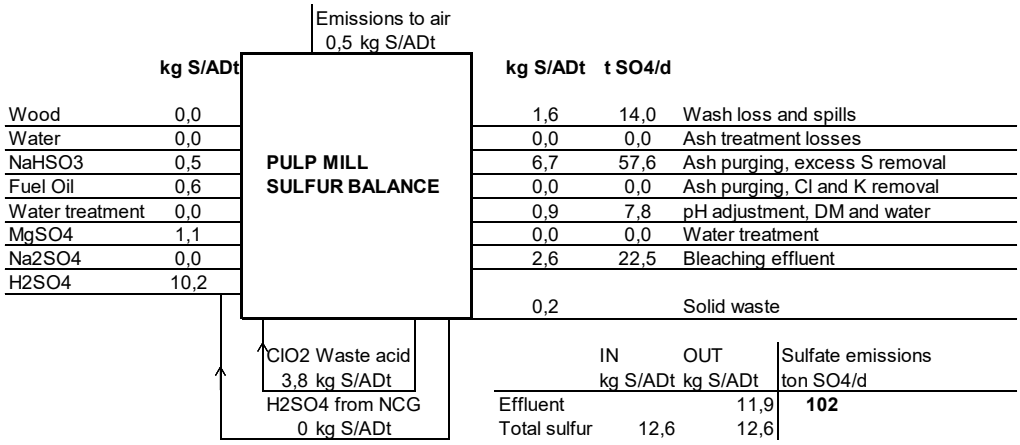

Figure 8. Sulfur balance when PAC is used in water treatment.

Table 7. Chemical consumptions when PAC is used in water treatment.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	283	g/ADt
Potassium In / Out	1565	g/ADt
Black liquor max Cl content	0.08	%wt
Black liquor max K content	1.03	%wt
Make-up chemicals		
Make-up NaOH	27.5	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	31.2	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8.3 Carbon dioxide as semi acidulation agent

The amount of sulfuric acid to tall oil production was estimated to be 220 kg/tonne of tall oil produced. It was estimated that 35% of sulfuric acid could be replaced with carbon dioxide (Table 8). The semi acidulation decreased the sulfur input, which reduced fly ash purging. The decrease of excess sulfur in Na/S-balance reduced the sulfate emissions from 119 to 108 t/d (Figure 9).

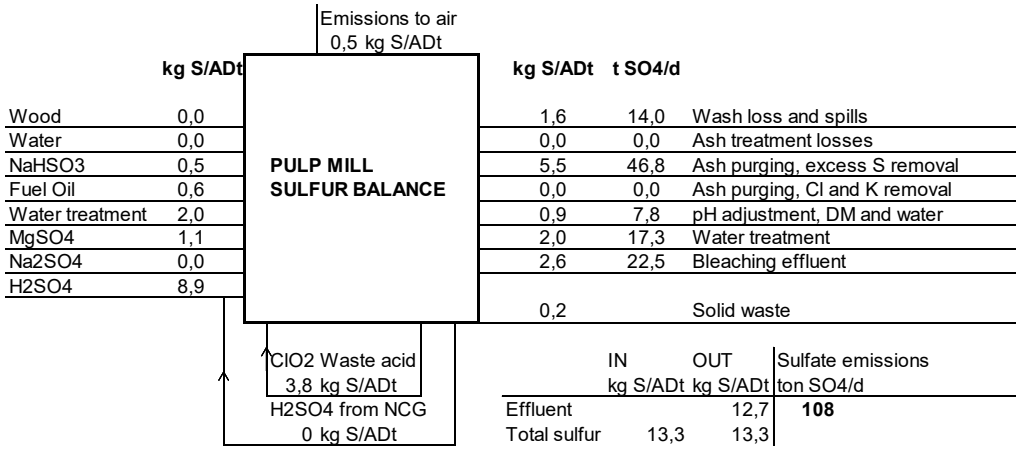

Figure 9. Sulfur balance with carbon dioxide as semi acidulation.

Table 8. Chemical consumption with CO_2 semi acidulation.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	265	g/ADt
Potassium In / Out	1561	g/ADt
Black liquor max Cl content	0.13	%wt
Black liquor max K content	1.20	%wt
Make-up chemicals		
Make-up NaOH	22.3	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	27.3	kg H_2SO_4/ADt
Tall Oil Splitting	7.15	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	69.1	kg CO_2/ ton of CTO

8.4 Integrated chlorine dioxide plant

The integrated chlorine dioxide plant (R6) includes chlorine dioxide plant, sodium chlorate plant, HCl plant and chlorine-alkali plant. The chlorine-alkali plant produces NaOH as a by-product, which is used as a make-up chemical. Since sulfuric acid is not used in the ClO_2 production, the sulfuric acid input decreases and no Na_2SO_4 by-product is generated.

Integrated chlorine dioxide plant led to lower amount of excess sulfur. Although the excess sulfur decreased, the fly ash was purged due to excess potassium in the Cl/K-balance. This led to make-up sodium sulfate consumption (Table 9). As Figure 10 describes, integrated ClO_2 plant decreased the sulfate emissions from 119 to 98 t/d.

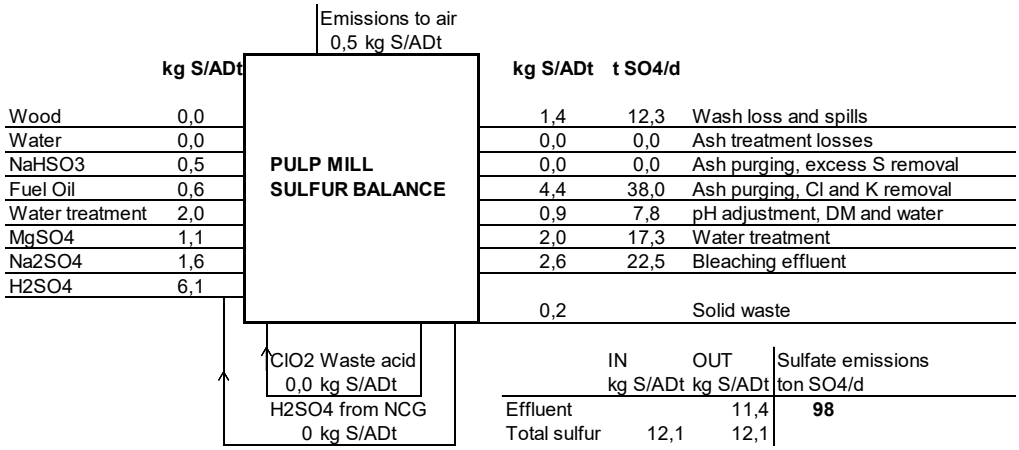

Figure 10. Sulfur balance with integrated chlorine dioxide plant.

Table 9. Chemical consumption with integrated chlorine dioxide plant.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	287	g/ADt
Potassium In / Out	1563	g/ADt
Black liquor max Cl content	0.17	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	23.6	kg NaOH/ADt
Make-up Na_2SO_4	6.9	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	18.8	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8.5 Ash Treatment

The selected ash treatment system was ash crystallization, since it requires no additional sulfuric acid and several industrial installations exists. The recovery and removal parameters are presented in Table 10.

Table 10. Recovery and removal parameters of ash crystallization.

Parameter	Efficiency %
Cl removal	90
K removal	87
Na recovery	85
S Recovery	90

Because fly ash was purged due to excess sulfur in the base case, there was no use for ash treatment. Therefore, the effect of ash treatment on sulfate emissions was calculated with integrated chlorine dioxide plant, since base case with integrated ClO_2 plant would lead to fly ash purging due to chloride content. It was concluded that the ash treatment led to better recovery of sodium and sulfur. The excess sulfur was removed with fly ash to maintain the Na/S-balance (Figure 11). The sulfate emissions with integrated ClO_2 plant and ash treatment were 85 t/d, which was 16 tons less than with ash purging. Table 11 compares the sulfate emissions and chemical consumptions with and without ash treatment.

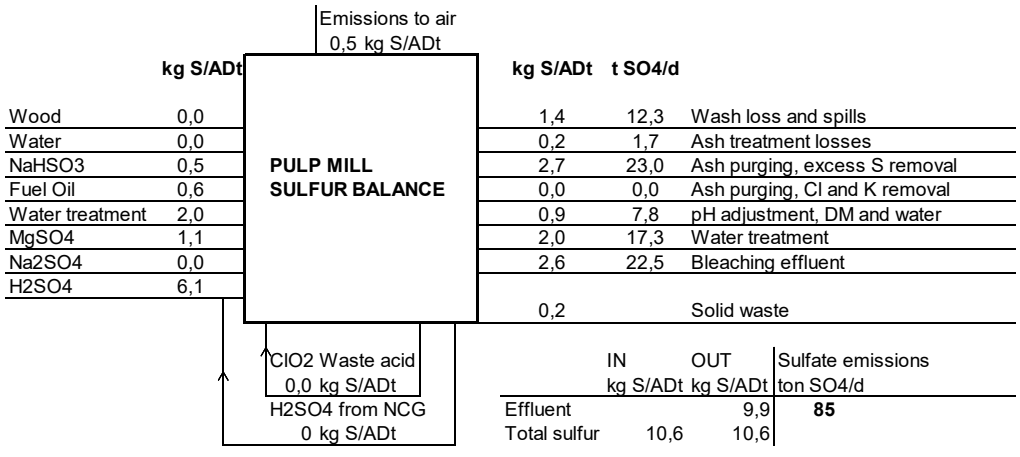

Figure 11. Sulfur balance of integrated chlorine dioxide plant with ash treatment.

Table 11. Comparison between ash purging and ash treatment.

Cl and K data	R6 and ash treatment	R6 and ash purging	
Treated ash	40.8	0.0	t/day
Chloride In / Out	251	287	g/ADt
Potassium In / Out	1561	1563	g/ADt
Black liquor max Cl content	0.15	0.17	%wt
Black liquor max K content	1.40	1.40	%wt
Make-up chemicals			
Make-up NaOH	22.0	23.6	kg NaOH/ADt
Make-up Na_2SO_4	0.0	6.9	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	18.8	18.8	kg H_2SO_4/ADt
Tall Oil Splitting	11	11	kg H_2SO_4/ADt
Bleaching	5.0	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	0.0	kg CO_2/ ton of CTO
Sulfate emissions	**85**	**101**	t SO_4/d

8.6 Sulfuric acid plant

It was estimated that all the CNCGs can be utilized in the sulfuric acid production, and DNCGs are used as a combustion air. The NCG flow described the capacity for the H_2SO_4 plant. The sulfuric acid plant was considered as an output of the Na/S-balance, because it decreased the excess sulfur in the recovery cycle. In the sulfur balance of the whole pulp mill area, the produced sulfuric acid generated an internal loop: the sulfur recovered from the NCGs was generated to sulfuric acid, which replaced the purchased acid.

Liquor heat treatment and green liquor stripping can be used to boost the NCG production, which enables higher capacity of the H_2SO_4 plant. However, it was concluded that there was no decrease in sulfate emissions if ash treatment was not included. Therefore, the effect of LHT and green liquor stripping was calculated

together with sulfuric acid plant and ash treatment. In order to get comparable results, sulfuric acid with ash treatment was calculated.

Figure 12 shows that the sulfuric acid plant without ash treatment decreased the sulfate emissions from 119 to 96 t/d. With ash treatment, the emissions were 76 t/d (Figure 13). Table 12 compares the effect of H_2SO_4 plant with and without ash treatment. The results showed that although the sulfuric acid plant is used to control the Na/S-balance, the Cl/K-balance may lead to ash removal (Figure 12). If ash treatment was used, the sulfate emissions decreased because of the enhanced recovery of sulfur (Figure 13). The sulfuric acid plant also reduced the make-up chemical consumption. Without ash treatment, Na_2SO_4 was used to replace the Na and S losses. With ash treatment the recovery cycle was more closed, and no Na_2SO_4 was required. Furthermore, the amount of make-up NaOH decreased (Table 12).

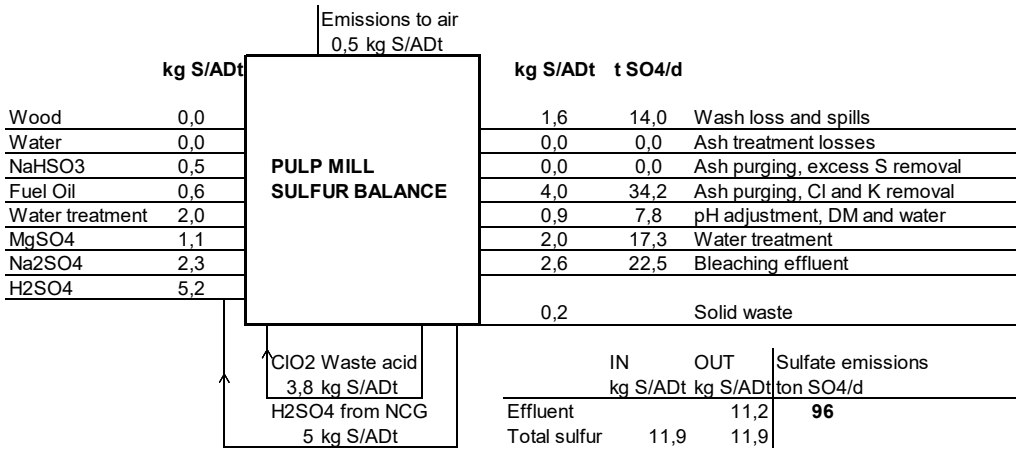

Figure 12. Sulfur balance of base case with sulfuric acid plant.

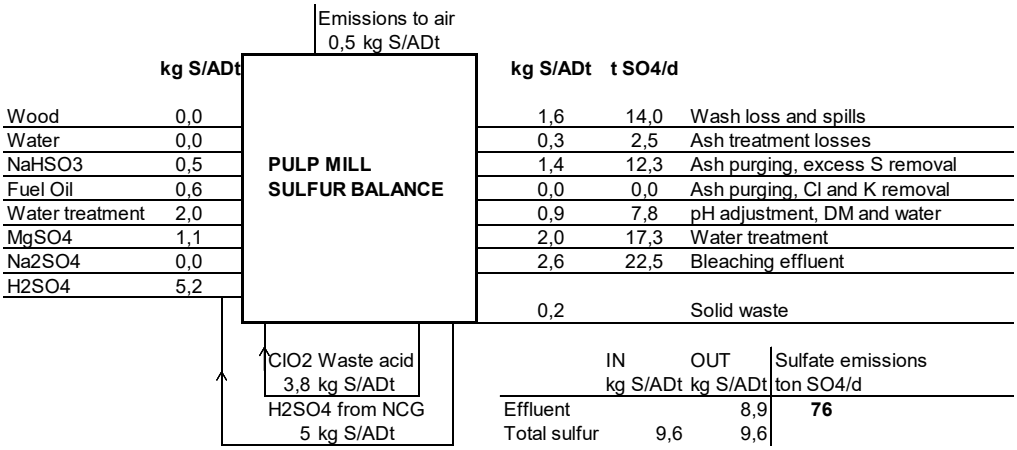

Figure 13. Sulfur balance of base case with sulfuric acid plant and ash treatment.

Table 12. The effect of H_2SO_4 plant on sulfate emissions and chemical consumption with and without ash treatment.

Cl and K data	H_2SO_4 plant with ash purging	H_2SO_4 plant with ash treatment	
Treated ash	0.0	65.4	t/day
Chloride In / Out	306	252	g/ADt
Potassium In / Out	1555	1552	g/ADt
Black liquor max Cl content	0.27	0.23	%wt
Black liquor max K content	1.40	1.40	%wt
Make-up chemicals			
Make-up NaOH	12.6	9.1	kg NaOH/ADt
Make-up Na_2SO_4	10.1	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	31.2	31.2	kg H_2SO_4/ADt
Tall Oil Splitting	11	11	kg H_2SO_4/ADt
Bleaching	5.0	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	0.0	kg CO_2/ ton of CTO
Sulfate emissions	**102**	**76**	t SO_4/d

8.6.1 Sulfuric acid plant with liquor heat treatment

Based on the literature, it was estimated that LHT increases the sulfur content in the NCGs by 2 kg S/ADt. Therefore, the total sulfur in NCGs with LHT was estimated to be 7 kg S/ADt. The LHT enabled higher capacity for internal sulfuric acid production, which decreased the sulfur input and output. Consequently, the sulfate emissions reduced from 76 to 66 t SO_4/d (Figure 14). The sulfuric acid plant closed the Na/S-balance, and the ash purge for excess sulfur removal was stopped. Since ash treatment resulted both sodium and sulfur losses, Na_2SO_4 was used as a make-up chemical (Table 13).

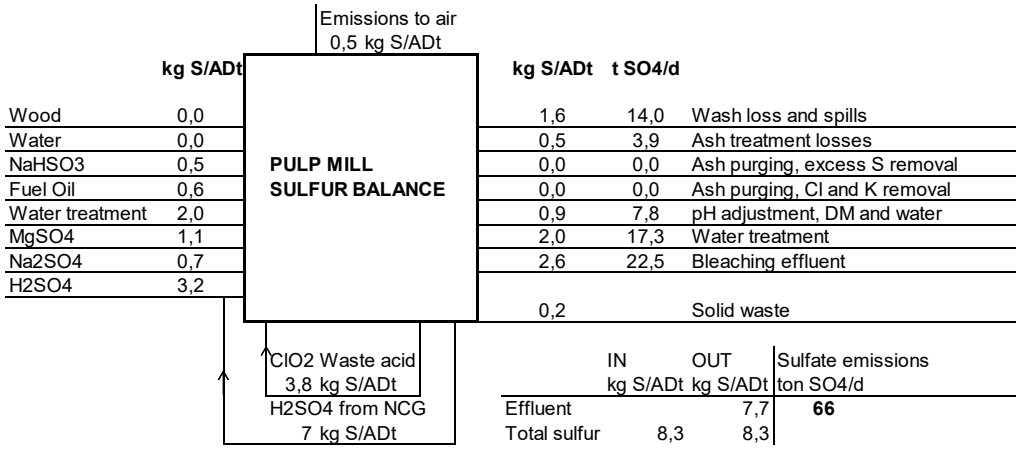

Figure 14. Sulfur balance of base case with sulfuric acid plant, ash treatment and LHT.

Table 13. Chemical consumption when H_2SO_4 plant capacity is increased with LHT.

Cl and K data		
Treated ash	101.3	t/day
Chloride In / Out	261	g/ADt
Potassium In / Out	1547	g/ADt
Black liquor max Cl content	0.24	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	2.2	kg NaOH/ADt
Make-up Na_2SO_4	3.2	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	31.2	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8.6.2 Green liquor stripping and carbonation

In the green liquor stripping and carbonation, part of sulfur is separated from green liquor in the form of H_2S by flue gas contact. The removed sulfur is oxidized to sulfuric acid, which is used in the various sulfuric acid consumers. The carbonation has an effect on liquor S/Na_2-ratio, since part of the sulfur in Na_2S is separated from

green liquor. The acid which is used in the tall oil plant or in the lignin separation (if used) is recovered to the liquor cycle. Therefore, green liquor stripping generates another sulfur cycle in addition to the main liquor cycle, presented in Figure 15 (dashed line). Since part of the sulfur is removed during the liquor cycle, it leads to higher S/Na_2-ratio in the recovery boiler than in the cooking plant. However, only small part of the green liquor is fed to stripping and carbonation.

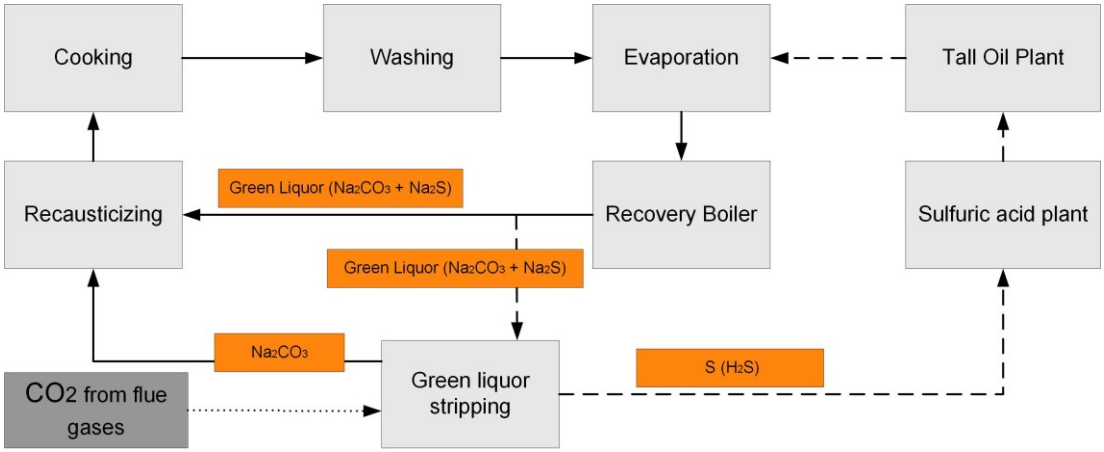

Figure 15. Effect of green liquor stripping to S/Na_2-ratio. Solid line describes the liquor cycle, and dashed line describes the sulfur cycle generated by green liquor stripping.

Green liquor stripping removed the excess sulfur from the Na/S-balance. Since part of sulfur was removed from the liquor cycle, sodium sulfate was used as a make-up. However, the amount of sodium remains the same in the liquor cycle. Since sodium sulfate includes both sodium and sulfur, Na_2SO_4 make-up decreased the make-up NaOH consumption. It was concluded that if the capacity of green liquor stripping and carbonation was increased, it led to the increase of liquor reserves since the sodium amount increased. Therefore, the capacity of green liquor carbonation was dimensioned that make-up NaOH flow is 0 kg/ADt.

With sulfuric acid plant and ash treatment the sulfur flow from carbonation to sulfuric acid plant was 2.7 kg S/ADt. The results were very close to LHT (Figure 16 and Table 14). The conclusion was that green liquor stripping and carbonation would be beneficial, if sulfuric acid is sold outside or there are high consumers, such as lignin separation.

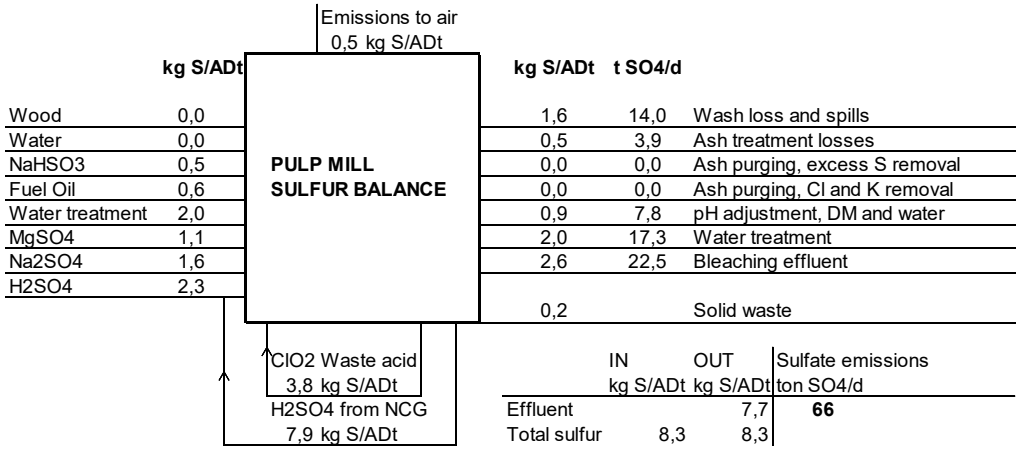

Figure 16. Sulfur balance with H_2SO_4 plant with green liquor carbonation. Ash treatment is included.

Table 14. Chemical consumptions with H_2SO_4 plant with green liquor carbonation. Ash treatment was included.

Cl and K data		
Treated ash	101.2	t/day
Chloride In / Out	279	g/ADt
Potassium In / Out	1546	g/ADt
Black liquor max Cl content	0.25	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	0.0	kg NaOH/ADt
Make-up Na_2SO_4	7.2	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	31.2	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

8.7 Bark gas as lime kiln fuel

Although bark gasification itself reduces no sulfate emissions, it has an indirect effect to the emissions. Heavy fuel oil for lime kiln contains sulfur, which increases the sulfur input in the Na/S-balance. When fuel oil is replaced by bark gas, the sulfur input decreased. However, since the bark gas includes potassium, the bark gasification may increase the potassium content in the recovery cycle, which may lead to the need for ash removal, which again increases sulfate emissions.

Several scenarios were calculated for bark gasification in order to investigate how the gasification affects to sulfate emissions. The scenarios are presented in Table 16. The calculations were based on the following initial data presented in Table 15.

Table 15. Bark and bark gas properties.

Lime kiln	
Production, average	869 ton/ d
Make-up CaO	29 ton/d
Fuel oil	
Lower Heating Value (LHV)	39.6 MJ/kg
Consumption	135 kg/ ton of lime
Bark gas	
Bark gas energy	85 MW
Bark moisture	10 %
Lower Heating Value	17.2 MJ/kg
Dry bark, mass flow	4 kg/s
Potassium in bark gas	2700 mg/kg

It was concluded that the bark gasification decreased the sulfate emissions in the base case. This was caused by the reduction of sulfur input, when fuel oil was not used. The rise of potassium content in the recovery cycle was not a problem, because the fly ash was still purged 40.4 kg/ADt to maintain the Na/S-balance. Simultaneously, the excess potassium was removed.

When the bark gasification was performed with sulfuric acid plant, there was only minor decrease in sulfate emissions. When compared to the scenario with base case and H_2SO_4 plant, the sulfate emissions increased from 96 t SO_4/d to 114 t SO_4/d due to removal of excess potassium. When ash treatment was added, the sulfate emissions decreased to 71 ton/d. The results are presented in Table 16.

Table 17 shows that bark gasification may also increase the sulfate emissions. If the sulfur balance was controlled with sulfuric acid plant and integrated ClO_2 plant, there was no excess sulfur in Na/S-balance. Furthermore, Cl/K-balance was maintained with ash treatment. In this situation the bark gasification increased the sulfate emissions, since the potassium content increased. That increased the need for ash purging, although sulfur input decreased.

Table 16. Results. The effect of bark gasification to sulfate emissions, when there was excess sulfur in Na/S-balance.

Case	**Gasification. Base Case**	**H_2SO_4 plant. Gasification**	**H_2SO_4 plant. Gasification. Ash treatment**	
Lime kiln fuel	Bark Gas	Bark Gas	Bark Gas	
Cl and K data				
Treated ash	0	0	115.1	t/day
Chloride In / Out	267	345	250	g/ADt
Potassium In / Out	1867	1861	1855	g/ADt
Black liquor max Cl %	0.10	0.26	0.07	%
Black liquor max K %	1.33	1.40	1.40	%
Fly Ash Purging				
Due to Na/S balance	42.7	0	4.6	kg/ADt
Due to Cl/K balance	0	39.6	0	kg/ADt
Make-up chemicals				
Make-up NaOH	24.8	13.4	7.4	kg NaOH/ADt
Make-up Na_2SO_4	0	17.8	0	kg Na_2SO_4/ADt
Sulfate emissions	**114**	**105**	**71**	**ton/d**

Table 17. Comparison of sulfate emissions with fuel oil and bark gas, when H_2SO_4 plant, integrated ClO_2 plant and ash treatment was used.

Lime kiln fuel **Cl and K data**	Heavy Fuel Oil	Bark Gas	
Treated ash	102	130	t/day
Chloride In / Out	293	309	g/ADt
Potassium In / Out	1551	1856	g/ADt
Black liquor max Cl content	0.26	0.23	%
Black liquor max K content	1.40	1.40	%
Fly Ash Purging			
Fly ash bleeding for Na/S balance	0	0.0	kg/ADt
Fly ash bleeding for Cl/K balance	0	0.0	kg/ADt
Make-up chemicals			
Make-up NaOH to be purchased	7.1	6.5	kg NaOH/ADt
Make-up Na_2SO_4 to be purchased	11.4	14.7	kg Na_2SO_4/ADt
Sulfate emissions	**64**	**65**	**ton/d**

9 Studied cases

The cases were calculated by combining the variables presented in the previous chapter. The aim of each case was to represent a feasible main dimensioning balance of a pulp mill with process design to reduce sulfate emissions. Chapter 8 concluded that PAC as a flocculating chemical and HCl as pH adjustment chemical reduced the fixed amount of sulfate emissions. Furthermore, these chemicals require no high investment costs. Therefore, these variables were automatically included in every case. Since ash purging seemed to be one of the primary sources of sulfate emissions, and several of the other variables had better efficiency when ash treatment was included, it was automatically included in the case of excess Cl or K. Also, bark gas was used as a lime kiln fuel in every case in order to reach the carbon neutrality.

9.1 Case 1 - Low cost investment

Case 1 required no major investments on sulfate load reduction; only process chemical changes in water treatment and pH adjustment were required. Two subcases were calculated: Case 1A with a conventional tall oil acidulation and Case 1B with CO_2 semi acidulation. This was done because the semi acidulation requires more investments to tall oil plant. Furthermore, in some situations the purchased CO_2 availability may be difficult due to mill location.

9.1.1 Case 1A – Low cost investment with conventional tall oil acidulation

Replacement of Al_2SO_4 by PAC in water treatment and H_2SO_4 by HCl in pH adjustment resulted in sulfate emissions of 75 t/d. When compared to the base case (119 t/d), the daily emissions decreased 44 tonnes. Based on the calculations presented in chapter 8, it can be estimated that the replacement of H_2SO_4 by HCl had the highest effect on sulfate load, 22 t/d, and the replacement of aluminum

sulfate by PAC decreased the sulfate emissions 17 t/d. The rest of the decrease was caused by bark gasification, since sulfur-containing fuel oil was not used. However, the balance had still excess sulfur, which was removed by ash purging. Because the ash purging controlled the Cl/K-balance, ash treatment was not required.

As Figure 17 describes, the majority of the sulfate emissions were originated from fly ash purging. The sulfate emissions from bleaching effluent decreased, since the H_2SO_4 was replaced in the bleach plant. The remaining emissions from bleach plant were originated from $NaHSO_3$ and $MgSO_4$.

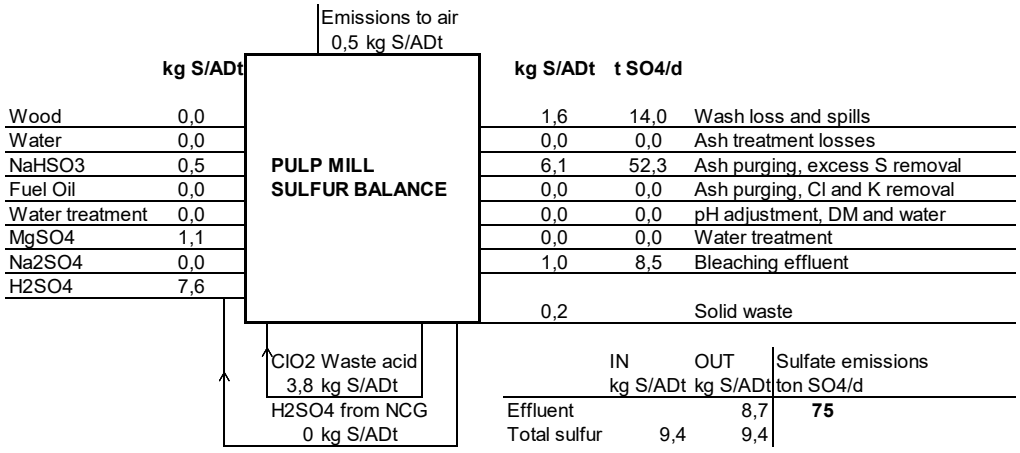

Figure 17. Sulfur balance of Case 1A

Table 18. Chemical consumptions of Case 1A

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	278	g/ADt
Potassium In / Out	1867	g/ADt
Black liquor max Cl content	0.12	%-wt
Black liquor max K content	1.36	%-wt
Make-up chemicals		
Make-up NaOH	23.8	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	23.4	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.1.2 Case 1B – Carbon dioxide semi acidulation

The semi acidulation decreased H_2SO_4 consumption in tall oil plant (Table 19). When compared to Case 1A, the ash purging due to sulfur removal decreased. Since the reduction of ash purging led to increased potassium content, ash treatment was required. However, the balance had still excess sulfur, which was removed by ash purging. The sulfate emissions of Case 1B were 64 t/d (Figure 18), which were 11 tons less than in Case 1A and 55 tons less than in the base case.

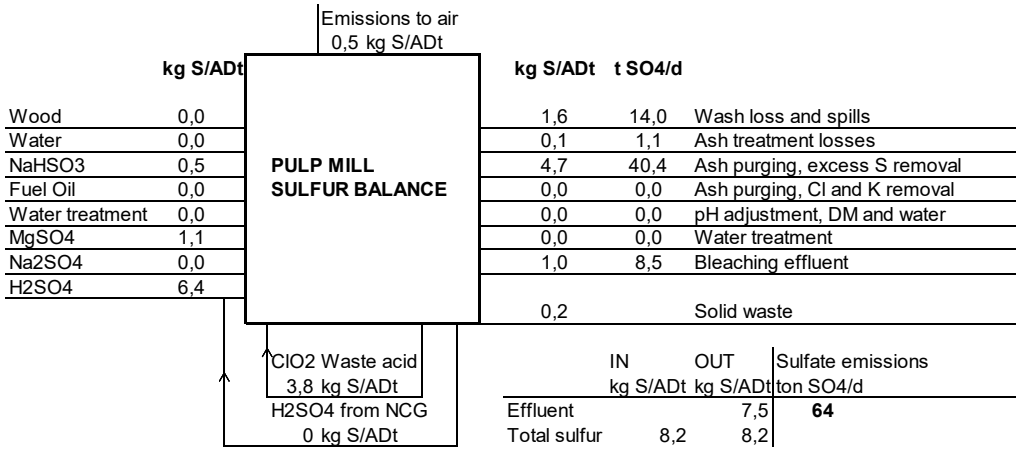

Figure 18. Sulfur balance of Case 1B.

Table 19. Chemical consumptions in Case 1B.

Cl and K data		
Treated ash	25.6	t/day
Chloride In / Out	274	g/ADt
Potassium In / Out	1864	g/ADt
Black liquor max Cl content	0.12	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	19.4	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	19.5	kg H_2SO_4/ADt
Tall Oil Splitting	7.15	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	69.1	kg CO_2/ ton of CTO

9.2 Case 2 – Sulfuric acid plant

In addition to the variables of Case 1A, Case 2 included sulfuric acid plant. Two sub-cases of Case 2 were calculated: Case 2A with 5 kg sulfur/ADt and Case 2B with LHT to increase the sulfuric acid production.

It was concluded, that H_2SO_4 plant with ash treatment made the sulfur balance more closed. The more closed sulfur cycle decreased the need for ash purging. The decrease of ash purging had two positive effects: reduction of sulfate emissions and lower make-up NaOH consumption.

9.2.1 5.1 Case 2A – Mill with internal sulfuric acid production

The sulfate emissions in Case 2A were 32 t/d (Figure 19). The reduction of sulfate emissions was caused by the decreased sulfur input and reduced amount of fly ash purging. However, the balance had still small amount of excess sulfur which was purged via fly ash. The sulfuric acid plant also decreased the NaOH consumption (Table 20).

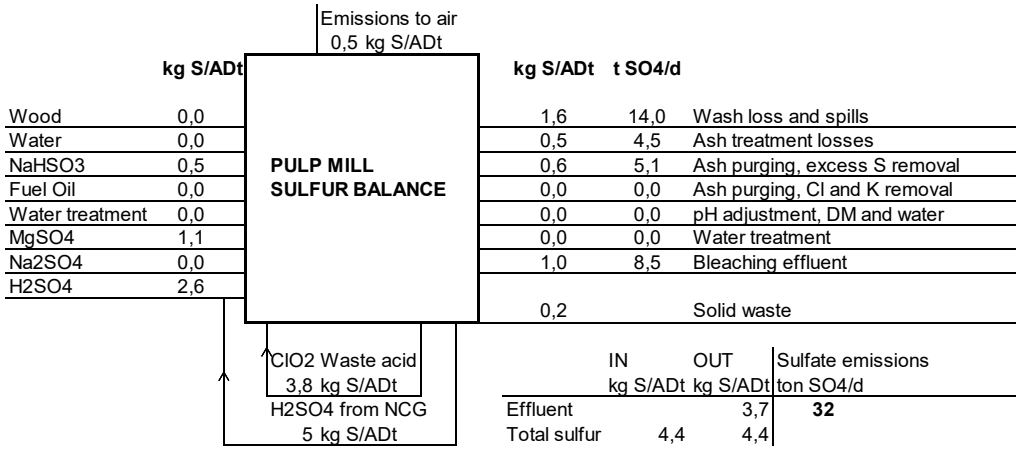

Figure 19. Sulfur balance of Case 2A.

Table 20. Chemical consumptions in Case 2A.

Cl and K data		
Treated ash	115.1	t/day
Chloride In / Out	262	g/ADt
Potassium In / Out	1855	g/ADt
Black liquor max Cl content	0.12	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	7.4	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	23.4	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.2.2 Case 2B – Sulfuric acid plant with LHT

It was estimated that LHT increases the sulfur content of NCGs from 5 kg S/ADt to 7 kg S/ADt. The increased sulfur content in NCGs increased the sulfuric acid production (Figure 20). The reduction of purchased H_2SO_4 decreased the sulfur input. The reduced sulfur input together with wash loss and ash treatment losses resulted in sulfur deficit. Therefore, Na_2SO_4 was used as a make-up chemical, which decreased the make-up NaOH consumption (Table 21). Sulfate emissions were 28 t/d (Figure 20).

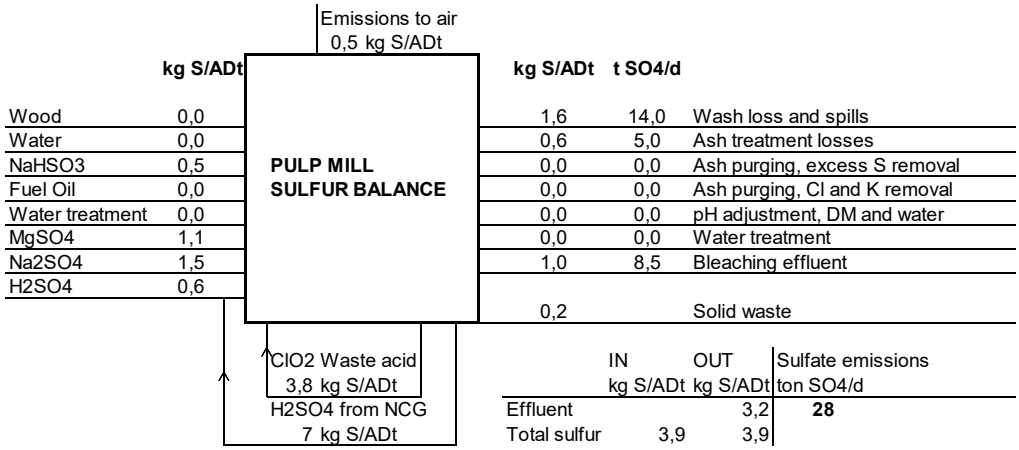

Figure 20. Sulfur balance of Case 2B.

Table 21. Chemical consumptions in Case 2B.

Cl and K data		
Treated ash	129.7	t/day
Chloride In / Out	289	g/ADt
Potassium In / Out	1852	g/ADt
Black liquor max Cl content	0.22	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	1.6	kg NaOH/ADt
Make-up Na_2SO_4	6.5	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	23.4	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.3 Case 3 – Integrated chlorine dioxide plant

Case 3 included the integrated (R6) chlorine dioxide plant. The plant included a HCl plant, which produced HCl for pH adjustment and for ClO_2 production. The excess NaOH from the chlorine-alkali-plant was utilized in the pulp mill. The only sulfuric acid consumer was the tall oil plant (Table 22 and Table 23). Two alternatives were

calculated, Case 3A with conventional tall oil acidulation and Case 3B with carbon dioxide semi acidulation.

9.3.1 Case 3A – Integrated chlorine dioxide plant with conventional acidulation

The sulfate emissions in Case 3A were 40 t/d (Figure 21). The reduction of sulfate emissions was caused by the decreased H_2SO_4 input. However, the sulfur balance had still excess sulfur, which was removed by fly ash purging.

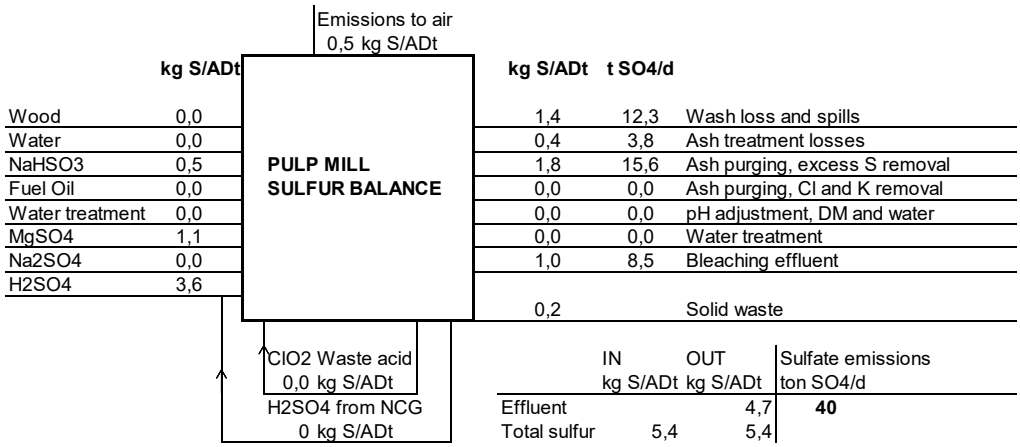

Figure 21. Sulfur balance of case 3A.

Table 22. Chemical consumptions of Case 3A.

Cl and K data		
Treated ash	88.9	t/day
Chloride In / Out	261	g/ADt
Potassium In / Out	1864	g/ADt
Black liquor max Cl content	0.11	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	20.4	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	11.0	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.3.2 Case 3B – Carbon dioxide semi acidulation

Semi acidulation decreased the sulfuric acid consumption, which decreased the excess sulfur. The daily sulfate emissions decreased to 29 tons. When compared to Case 3A, more fly ash was led to ash treatment, which led to more sulfur losses from ash treatment (Figure 22). However, the decreased excess sulfur lowered the sulfate emissions.

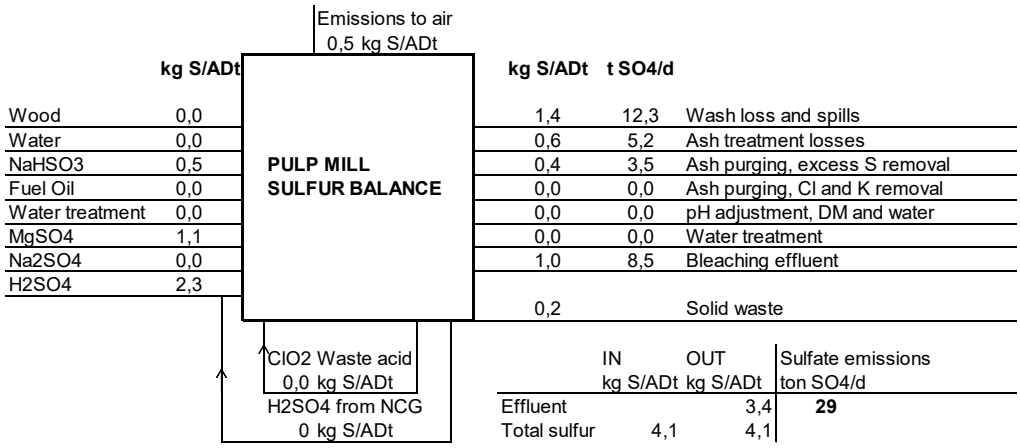

Figure 22. Case 3 with bark gasification and CO2 semi acidulation.

Table 23. Chemical consumptions of Case 3B.

Cl and K data		
Treated ash	121.3	t/day
Chloride In / Out	257	g/ADt
Potassium In / Out	1861	g/ADt
Black liquor max Cl content	0.09	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	16.0	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	7.2	kg H_2SO_4/ADt
Tall Oil Splitting	7.15	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	69.1	kg CO_2/ ton of CTO

9.4 Case 4 – Sulfuric acid plant and integrated ClO_2 plant

Case 4 included internal sulfuric acid plant and integrated chlorine dioxide plant. As concluded in Chapter 7.7, bark gasification can also increase the sulfate emissions in case of no fly ash is purged. Therefore, Case 4 was calculated with bark gasification and with fuel oil as lime kiln fuel. Case 4A presented the bark gasification option, whereas in Case 4B fuel oil was used as a lime kiln fuel.

9.4.1 Case 4A

The sulfur balance was closed by sulfuric acid plant in case 4A. Furthermore, integrated chlorine dioxide plant decreased the sulfur input. Since tall oil plant was the only consumer for sulfuric acid, the acid production was limited. Therefore, 3.6 kg S/ADt from NCGs were utilized in sulfuric acid production, whereas the remaining amount of the NCGs was incinerated in the NCG incinerator. Otherwise the sulfuric acid plant would produce more acid than required. Another option would be to sell the excess H_2SO_4. However, the profitability of selling the acid is dependent on the mill location, and quality and production amount of the acid. The sulfate emissions decreased to 26 t/d (Figure 23). Since there was a deficit of sulfur in Na/S-balance, Na_2SO_4 was used as a make-up chemical (Table 24).

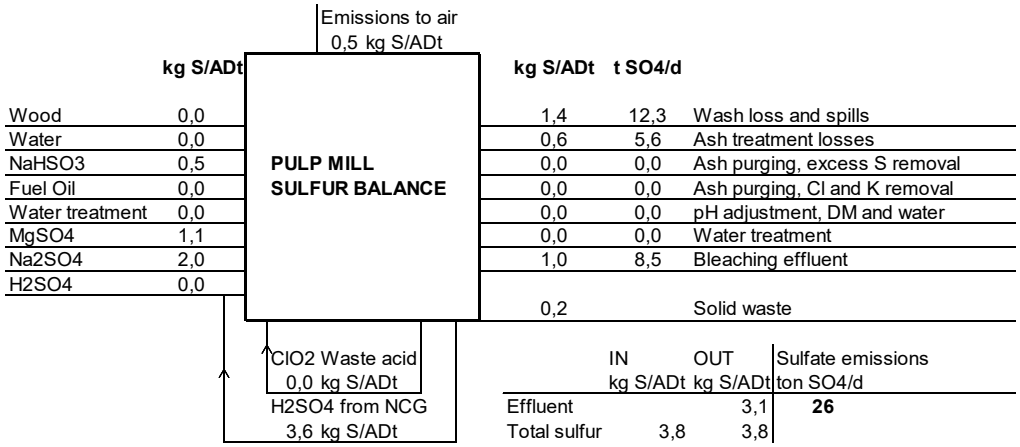

Figure 23. Sulfur balance of Case 4A

Table 24. Chemical consumptions of Case 4A.

Cl and K data		
Treated ash	130.3	t/day
Chloride In / Out	294	g/ADt
Potassium In / Out	1858	g/ADt
Black liquor max Cl content	0.14	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	9.7	kg NaOH/ADt
Make-up Na_2SO_4	8.8	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	11.0	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.4.2 Case 4B

Case 4B was calculated with heavy fuel oil as lime kiln fuel. Since the Na/S-balance had deficit of sulfur in Case 4, an increased sulfur input with lime kiln fuel decreased the make-up Na_2SO_4 consumption (Table 25). Furthermore, switching the bark gasification to fuel oil decreased the amount of treated ash, since the potassium

input decreased. The sulfate emissions dropped since the ash treatment losses were decreased (Figure 24).

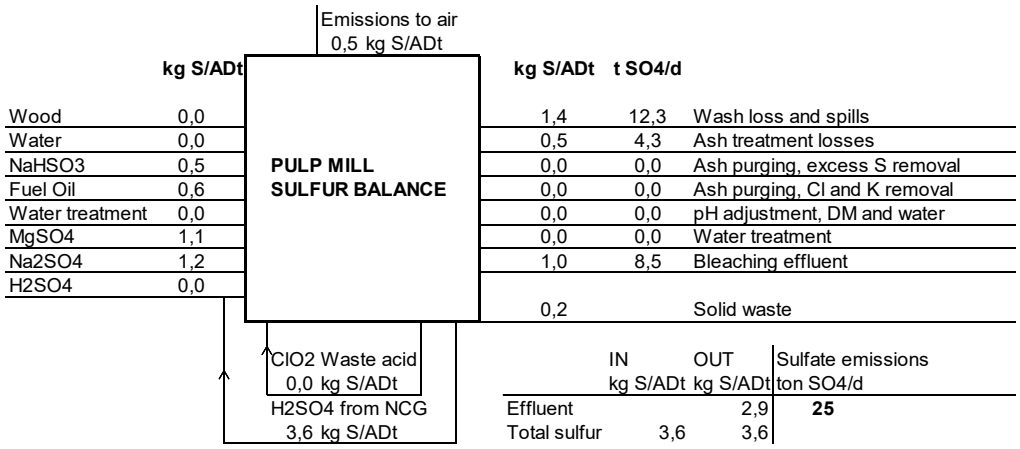

Figure 24. Sulfur balance of Case 4B.

Table 25. Chemical consumptions of Case 4B.

Cl and K data		
Treated ash	102.0	t/day
Chloride In / Out	278	g/ADt
Potassium In / Out	1553	g/ADt
Black liquor max Cl content	0.16	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	10.5	kg NaOH/ADt
Make-up Na_2SO_4	5.4	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	11.0	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

9.5 Case 5 – Reduction of sulfate emissions with lignin separation

The hypothesis was that since lignin separation increases sulfuric acid consumption, it also increases the sulfate emissions. It was estimated that 135 kg of lignin can be

separated per ton of pulp. The estimated sulfuric acid consumption was 190 kg H_2SO_4/ton of lignin. First it was calculated how the sulfate emissions were increased when compared to the base case. Figure 25 represented the sulfur balance when lignin separation was included. Sulfate emissions increased to 189 t/d, which was 70 t/d more than in the base case. Also, the amount of make-up NaOH was high (Table 26).

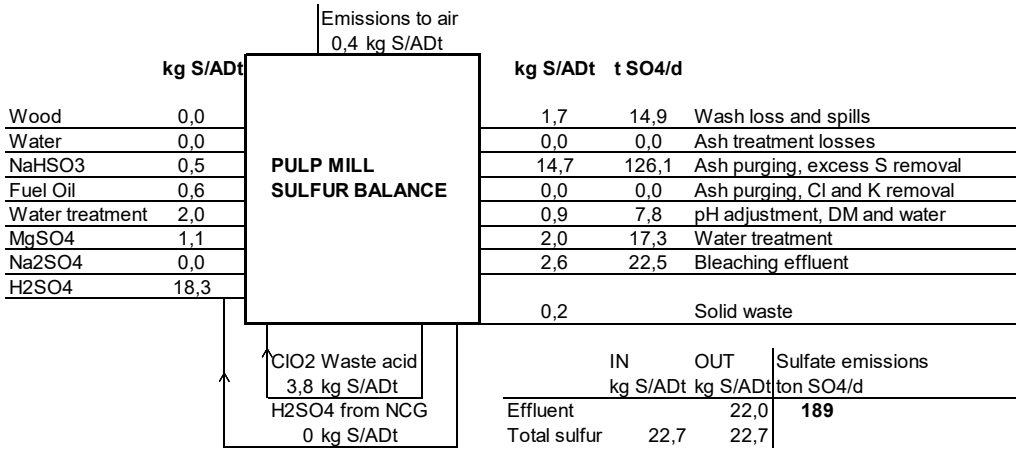

Figure 25. Base case with lignin separation.

Table 26. Chemical consumptions of base case with lignin separation.

Cl and K data		
Treated ash	0.0	t/day
Chloride In / Out	316	g/ADt
Potassium In / Out	1588	g/ADt
Black liquor max Cl content	0.10	%wt
Black liquor max K content	0.51	%wt
Make-up chemicals		
Make-up NaOH	61.3	kg NaOH/ADt
Make-up Na_2SO_4	0.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	55.9	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	5.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	12.4	kg H_2SO_4/ADt
Drying Machine and Water Treatment	2.8	kg H_2SO_4/ADt
Lignin separation	24.7	kg H_2SO_4/ADt
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

It was observed that in order to control the sulfate emissions with lignin plant, several reduction methods for sulfate emissions were required. Therefore, integrated chlorine dioxide plant and internal sulfuric acid plant was included to Case 5. However, the sulfur content of NCGs limited the capacity of H_2SO_4 plant. When the sulfur content in NCGs was 5 kg S/ADt, it represented 15.2 kg of sulfuric acid produced, whereas lignin separation required 24.7 kg H_2SO_4/ADt. Therefore, green liquor stripping and carbonation was selected to increase the capacity of sulfuric acid plant.

The capacity of green liquor stripping unit was selected to be 5 kg S/ADt. Therefore, the sulfur from green liquor stripping and NCG collection together was 10 kg S/ADt. As concluded in the chapter 8.6.2, the green liquor stripping and carbonation has an effect to S/Na_2-ratio of the liquor. It was calculated that if 5 kg of sulfur/ADt was removed during the green liquor stripping, the S/Na_2-ratio increased from 0.38 to 0.39 in the recovery boiler.

It was concluded that the increased H_2SO_4 production removed the excess sulfur. The results showed that the increased sulfuric acid production with integrated chlorine dioxide plant, HCl as a pH adjustment chemical and PAC as a coagulation chemical decreased the sulfate emissions to 26 t/d. Since the base case with lignin separation had the sulfate emissions of 189 t/d, the reduction was significant.

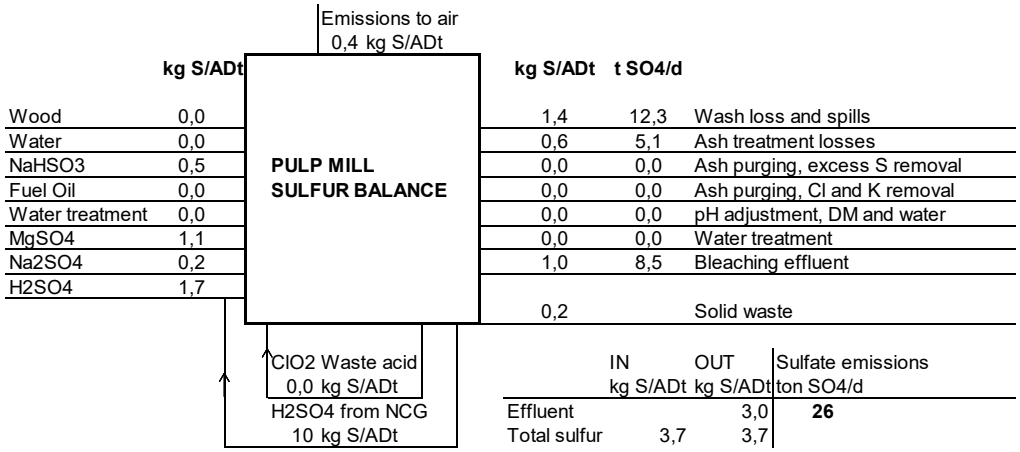

Figure 26. Sulfuric acid plant of Case 5.

Table 27. Chemical consumptions of case 5.

Cl and K data		
Treated ash	130.6	t/day
Chloride In / Out	260	g/ADt
Potassium In / Out	1860	g/ADt
Black liquor max Cl content	0.10	%wt
Black liquor max K content	1.40	%wt
Make-up chemicals		
Make-up NaOH	14.2	kg NaOH/ADt
Make-up Na_2SO_4	1.0	kg Na_2SO_4/ADt
Sulfuric acid consumption, total	35.7	kg H_2SO_4/ADt
Tall Oil Splitting	11	kg H_2SO_4/ADt
Bleaching	0.0	kg H_2SO_4/ADt
Chlorine Dioxide Plant	0.0	kg H_2SO_4/ADt
Drying Machine and Water Treatment	0.0	kg H_2SO_4/ADt
Lignin separation	24.7	
Carbon dioxide to tall oil plant	0.0	kg CO_2/ ton of CTO

10 Summary

The results of this thesis show that the sulfate emissions can be reduced by decreasing sulfur input, replacing sulfate-based chemicals by other chemicals and closing the sulfur balance. Integrated ClO_2 plant and CO_2 semi acidulation in tall oil plant decreased the sulfur input. Sulfuric acid plant and ash treatment made the Na/S-balance more closed. The replacement of H_2SO_4 by HCl in pH adjustment and aluminum sulfate by PAC reduced the sulfate emissions in effluent. Figure 27 represents the formation of sulfate emissions and solutions to reduce the emissions.

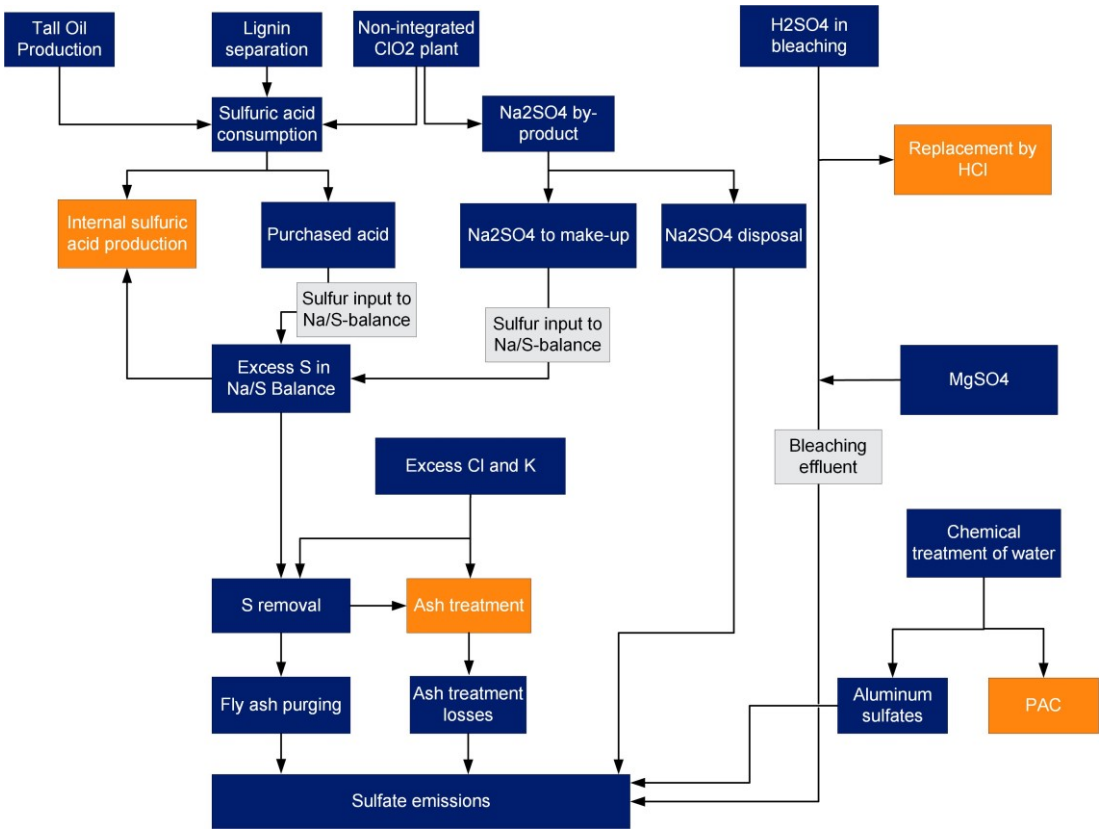

Figure 27. Causalities of sulfate emissions. Orange boxes represents the main reduction methods of sulfate emissions.

Table 28 summarizes the sulfate emissions, make-up chemicals and purchased sulfuric acid in cases 0–5. In comparison to Case 0, the amount of purchased acid decreased in cases 1 and 3, since the acid consumption was decreased. In Cases 2,

4 and 5 the acid was produced internally in addition to lower acid demand. The results of this thesis show that Cases 4 and 5 had the lowest sulfate emissions. Although lignin separation increased sulfuric acid consumption and sulfate emissions, Case 5 had roughly the same sulfate load as Case 4, since green liquor stripping and carbonation was applied. However, the sulfate emissions in Case 2B were almost as low in Case 4A, and the make-up chemical consumption of cases 2A and 2B was lower than in other cases.

Table 28. Summary of Cases 0-5.

Case	**Make-up NaOH** kg/ADt	**Make-up Na_2SO_4** kg/ADt	**Purchased H_2SO_4** kg/ADt	**Sulfate emissions** ton SO_4/d
0	25.1	0	31.2	119
1A	23.8	0	23.4	75
1B	19.4	0	19.5	64
2A	7.4	0	8.1	32
2B	2.6	6.5	2.0	28
3A	20.4	0.0	11	40
3B	16.0	0	7.2	29
4A	9.7	8.8	0	26
4B	10.5	5.4	0	25
5	14.2	1.0	5.1	26

Since the study was limited to greenfield mills, the results cannot be straightforwardly compared to existing pulp mills. Today tertiary treatment is not often used in pulp mills, and if it is performed with aluminum sulfate, it increases the sulfate emissions. Therefore, the sulfate emissions of a conventional pulp mill with the same production capacity could be slightly less than in the base case.

It can be concluded that the reduction of sulfate emissions also decreases the make-up chemical consumption. If HCl is used to replace sulfuric acid, the risk of corrosion increases. Also, HCl increases the chloride amount in effluent. If the bleach filtrate is circulated to brown stock washing, it may increase the chloride content in the recovery cycle. Further research should focus on determining the effect of increased chloride content in effluent.

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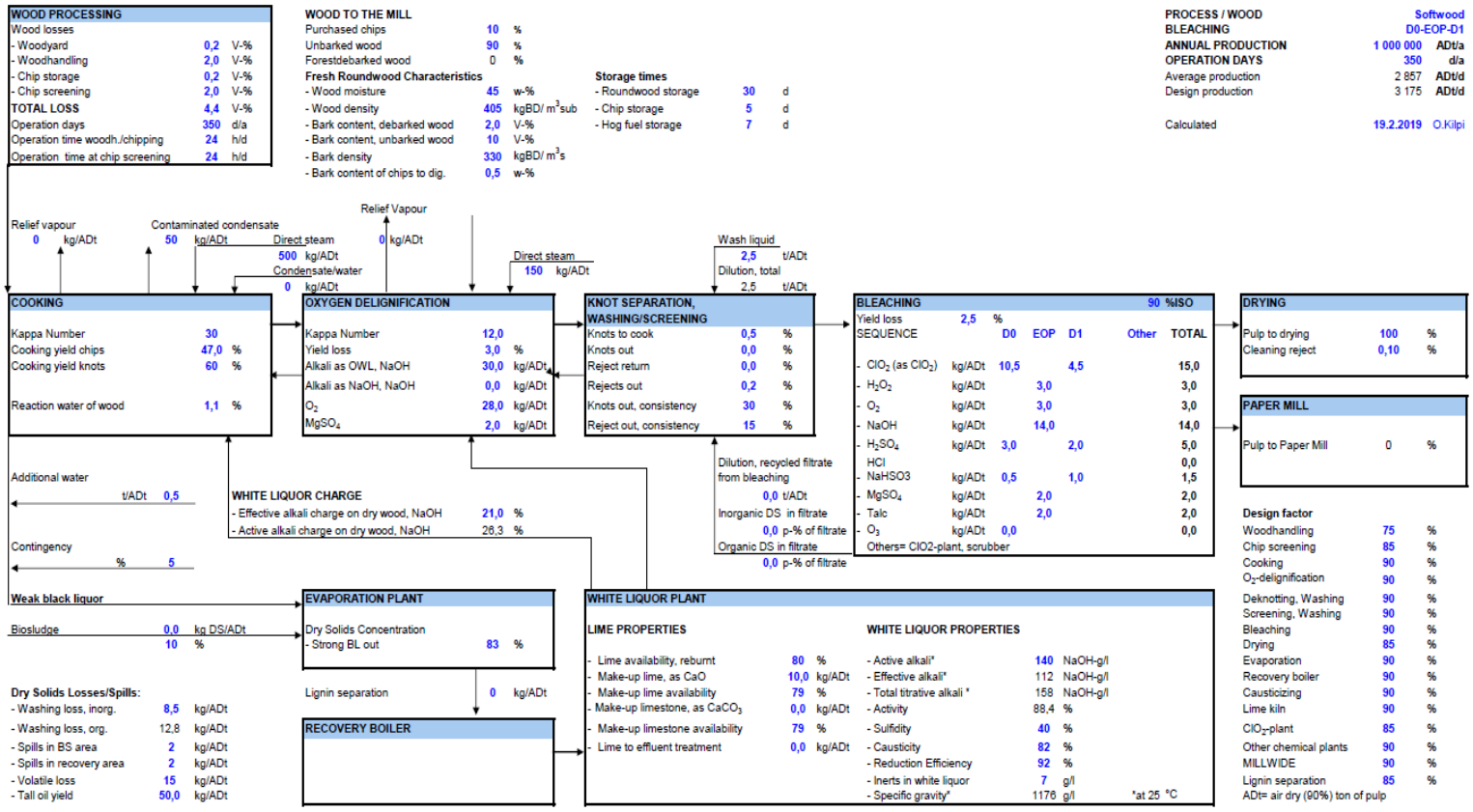
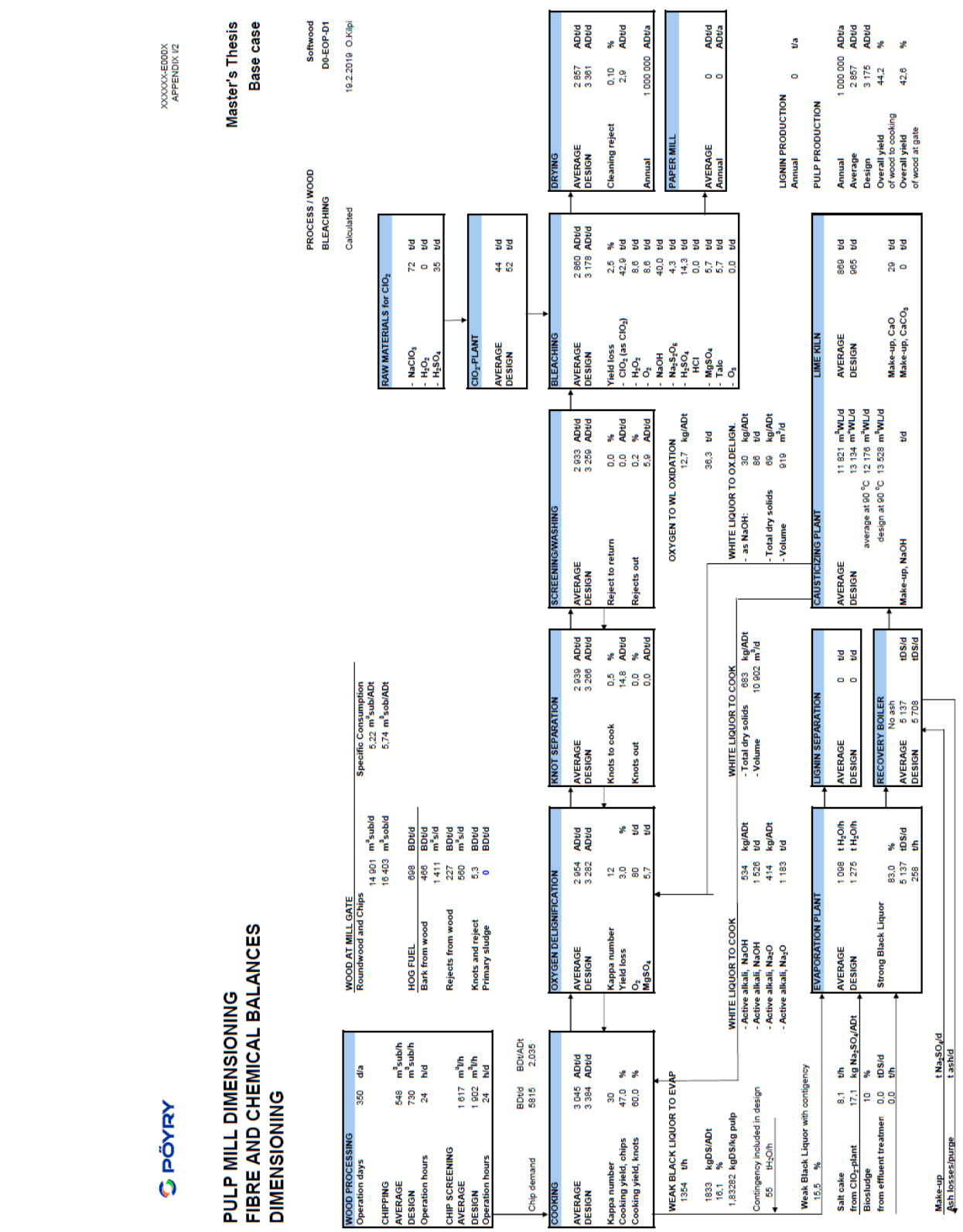
PULP MILL MAIN DIMENSIONING
FIBRE AND CHEMICAL BALANCES
INPUT VALUES

Master's Thesis
Base case

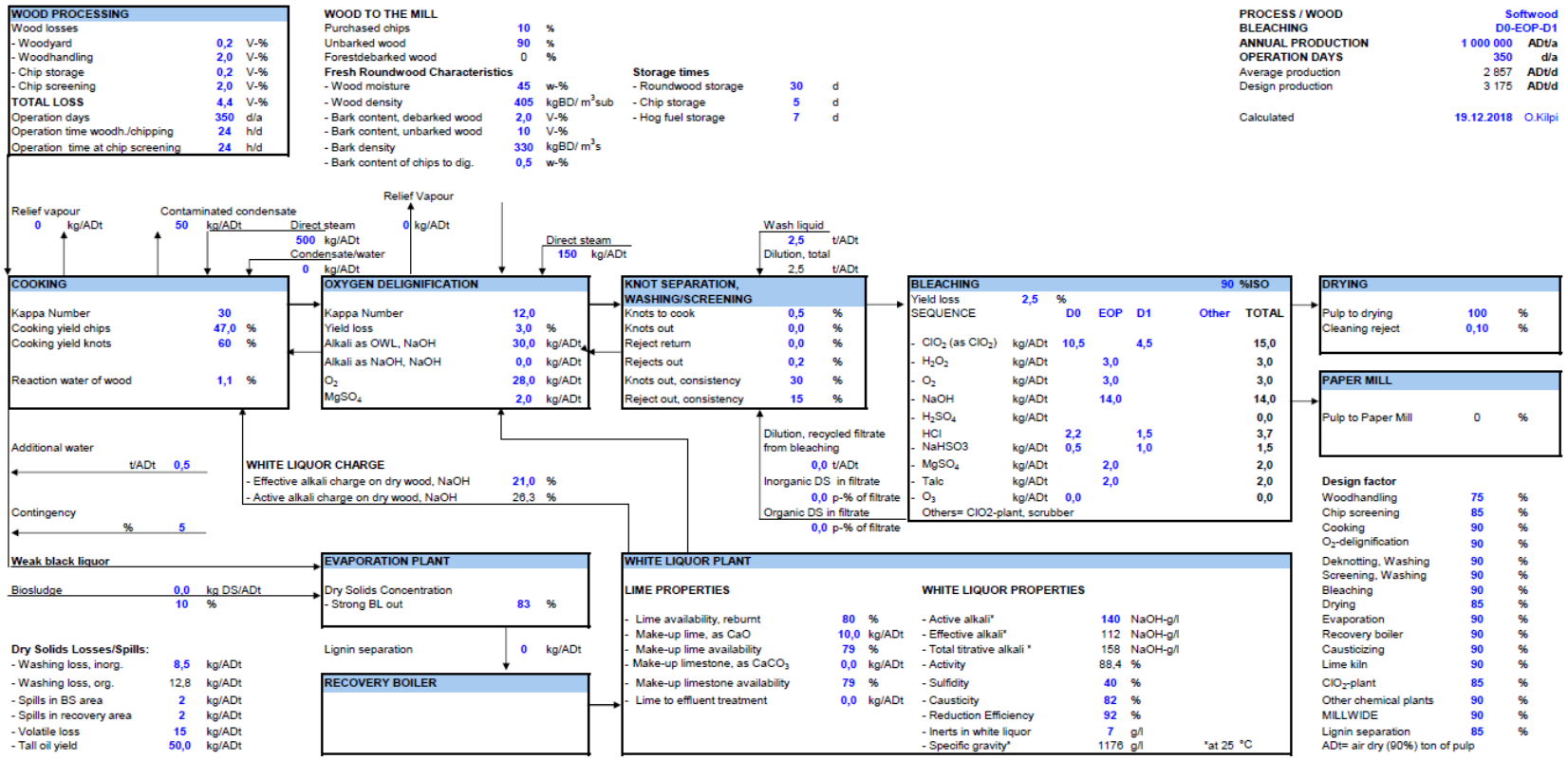


Appendix 2. Fibre and chemical balances for Case 0.

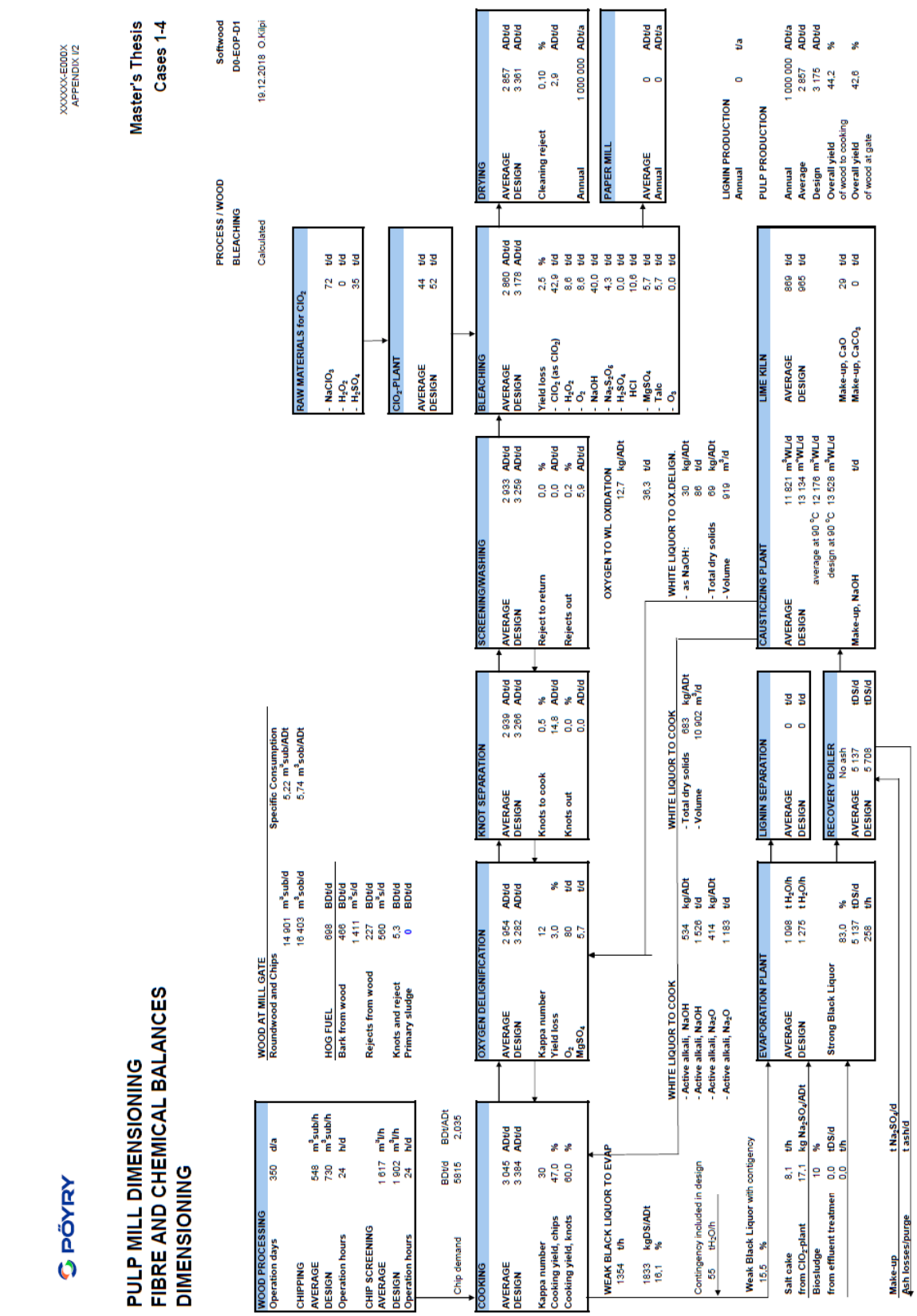


PULP MILL MAIN DIMENSIONING
FIBRE AND CHEMICAL BALANCES
INPUT VALUES

Master's Thesis
Cases 1-4



Appendix 4. Fibre and chemical balances for cases 1–5.



PULP MILL MAIN DIMENSIONING
FIBRE AND CHEMICAL BALANCES
INPUT VALUES

Master's Thesis
Case 5

PROCESS / WOOD		**Softwood**
BLEACHING		**D0-EOP-D1**
ANNUAL PRODUCTION	**1 000 000**	**ADt/a**
OPERATION DAYS	**350**	**d/a**
Average production	2 857	**ADt/d**
Design production	3 175	**ADt/d**
Calculated	**19.12.2018**	O.Kilpi

WOOD PROCESSING

Wood losses		
- Woodyard	0,2	V-%
- Woodhandling	2,0	V-%
- Chip storage	0,2	V-%
- Chip screening	2,0	V-%
TOTAL LOSS	4,4	V-%
Operation days	350	d/a
Operation time woodh./chipping	24	h/d
Operation time at chip screening	24	h/d

WOOD TO THE MILL

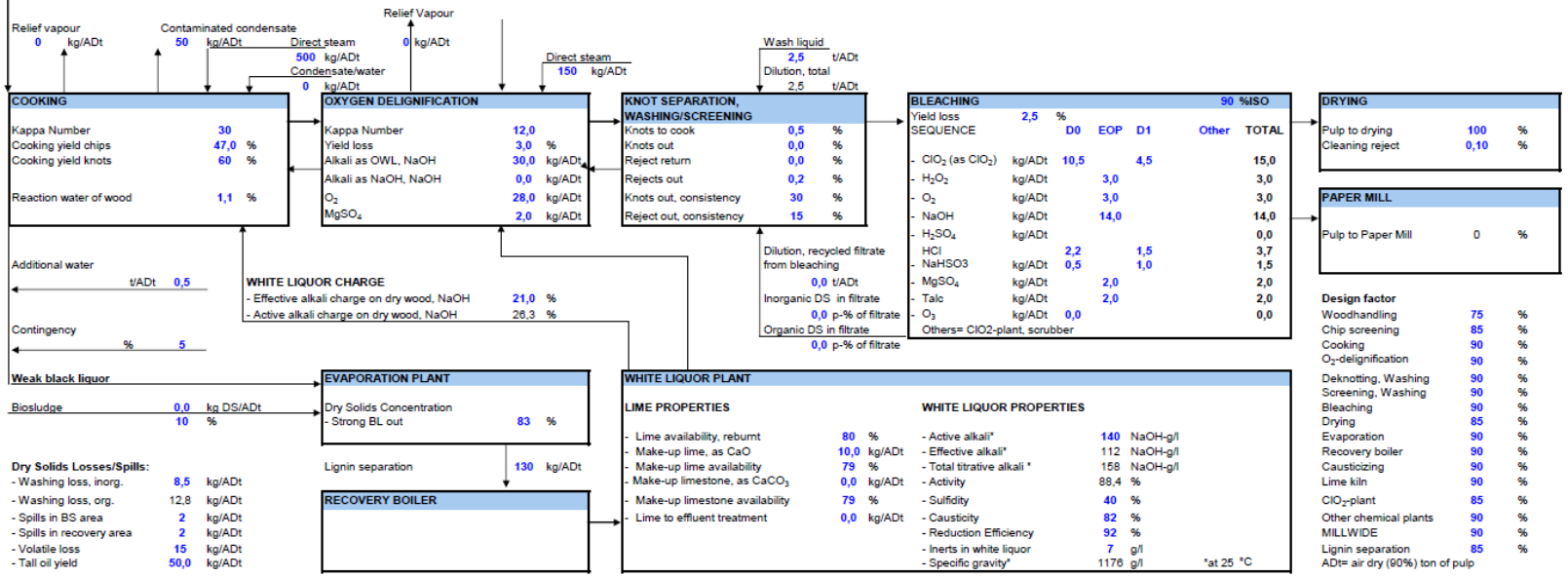
Purchased chips	10	%
Unbarked wood	90	%
Forestdebarked wood	0	%

Fresh Roundwood Characteristics

- Wood moisture	45	w-%
- Wood density	405	kgBD/ m^3sub
- Bark content, debarked wood	2,0	V-%
- Bark content, unbarked wood	10	V-%
- Bark density	330	kgBD/ m^3s
- Bark content of chips to dig.	0,5	w-%

Storage times

- Roundwood storage	30	d
- Chip storage	5	d
- Hog fuel storage	7	d



Dry Solids Losses/Spills:

- Washing loss, inorg.	8,5	kg/ADt
- Washing loss, org.	12,8	kg/ADt
- Spills in BS area	2	kg/ADt
- Spills in recovery area	2	kg/ADt
- Volatile loss	15	kg/ADt
- Tall oil yield	50,0	kg/ADt

Design factor

Woodhandling	75	%
Chip screening	85	%
Cooking	90	%
O_2-deligni fication	90	%
Deknotting, Washing	90	%
Screening, Washing	90	%
Bleaching	90	%
Drying	85	%
Evaporation	90	%
Recovery boiler	90	%
Causticizing	90	%
Lime kiln	90	%
ClO_2-plant	85	%
Other chemical plants	90	%
MILLWIDE	90	%
Lignin separation	85	%

ADt= air dry (90%) ton of pulp

Appendix 6. Fibre and chemical balances for Case 5